CHARACTERIZATION OF NANOSTRUCTURES BY FTIR SPECTROSCOPIES

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NANOMATERIAL CLASSES AND THEIR DIMENSIONALITY

Dimensionality	Classes		
	Class 1 Discrete nano-objects	Class 2 Surface nano-featured materials	Class 3 Bulk nano-structured materials
0-D All 3 dimensions on nano scale	Nanoparticles *(smoke, diesel fumes)*	Nanocrystalline films	Nanocrystalline materials Nanoparticle composites
1-D 2 dimensions on nano scale	Nanorods and tubes *(carbon nano tubes)*	Nano interconnects	Nanotube-reinforced composites
2-D 1 dimension on nano scale	Nanofilms, foils *(gilding foil)*	Nano surface layers	Multilayer structures

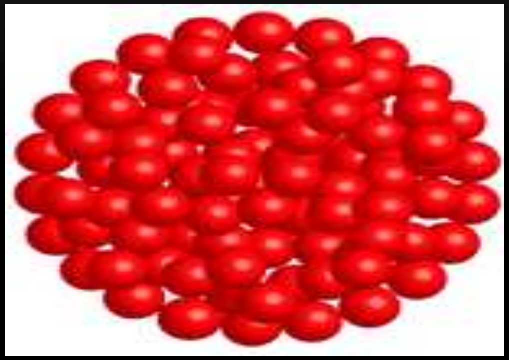
Quantum confinement in semiconductors

- In an unconfined (bulk) semiconductor, an electron-hole pair is typically bound within a characteristic length called the Bohr exciton radius.
- If the electron and hole are constrained further, then the semiconductor's properties change.
- This effect is a form of quantum confinement.
- Quantum confinement is a key feature in many emerging electronic structures.

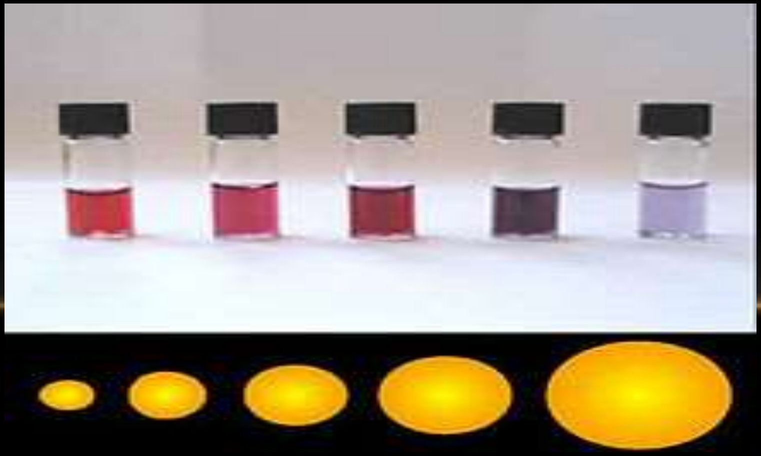
An exciton is a bound state of an electron and an imaginary particle called an electron hole in an insulator or semiconductor, and such is a Coulomb-correlated electron-hole pair

Some Nano-Definitions

Cluster: A collection of units (atoms or reactive molecules) of up to about 50 units.

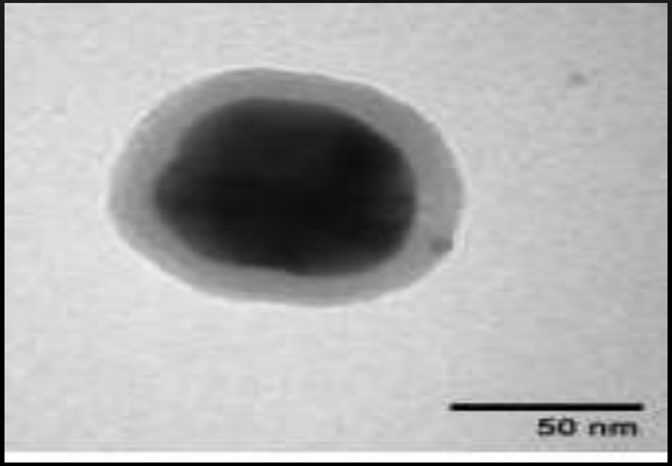


Colloids: A stable liquid phase containing particles in the 1-1000 nm range.

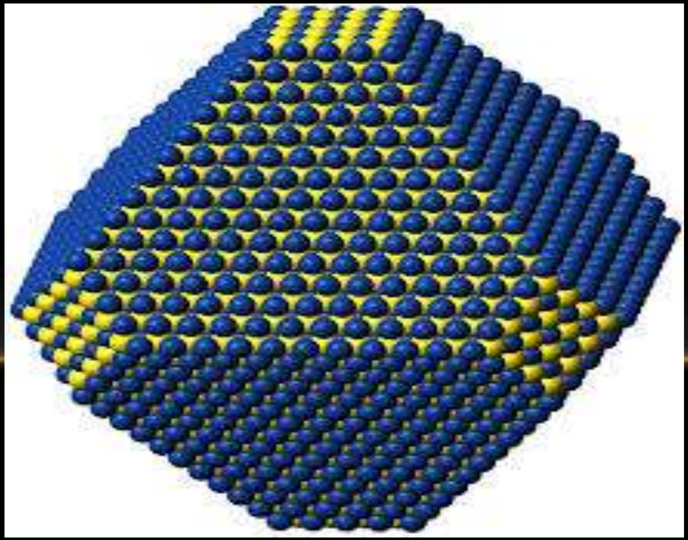


Suspensions of gold nanoparticles of various sizes. The size difference causes the difference in colors.

Nanoparticle: A solid particle in the 1-100 nm range that could be nanocrystalline, an aggregate of crystallite or a single crystallite.



Nanocrystal: A solid particle that is a single crystal in the nanometer range.



The Nano-size affects many properties such as

- Melting point
- Boiling point
- Band gap
- Optical properties
- Electrical properties
- Magnetic properties

Nanoscale materials are divided into three category

1. **Zero dimension** – length , breadth and heights are confined at single point. (for example, Nano dots)
2. One dimension – It has only one parameter either length (or) breadth (or) height (example: very thin surface coatings)
3. Two dimensions - It has only length and breadth (for example, nanowires and nanotubes)
4. **Three dimensions** - It has all parameter of length, breadth and height. (for example, Nano Particles).

Based on the size and shape, the Nano materials are classified as follows

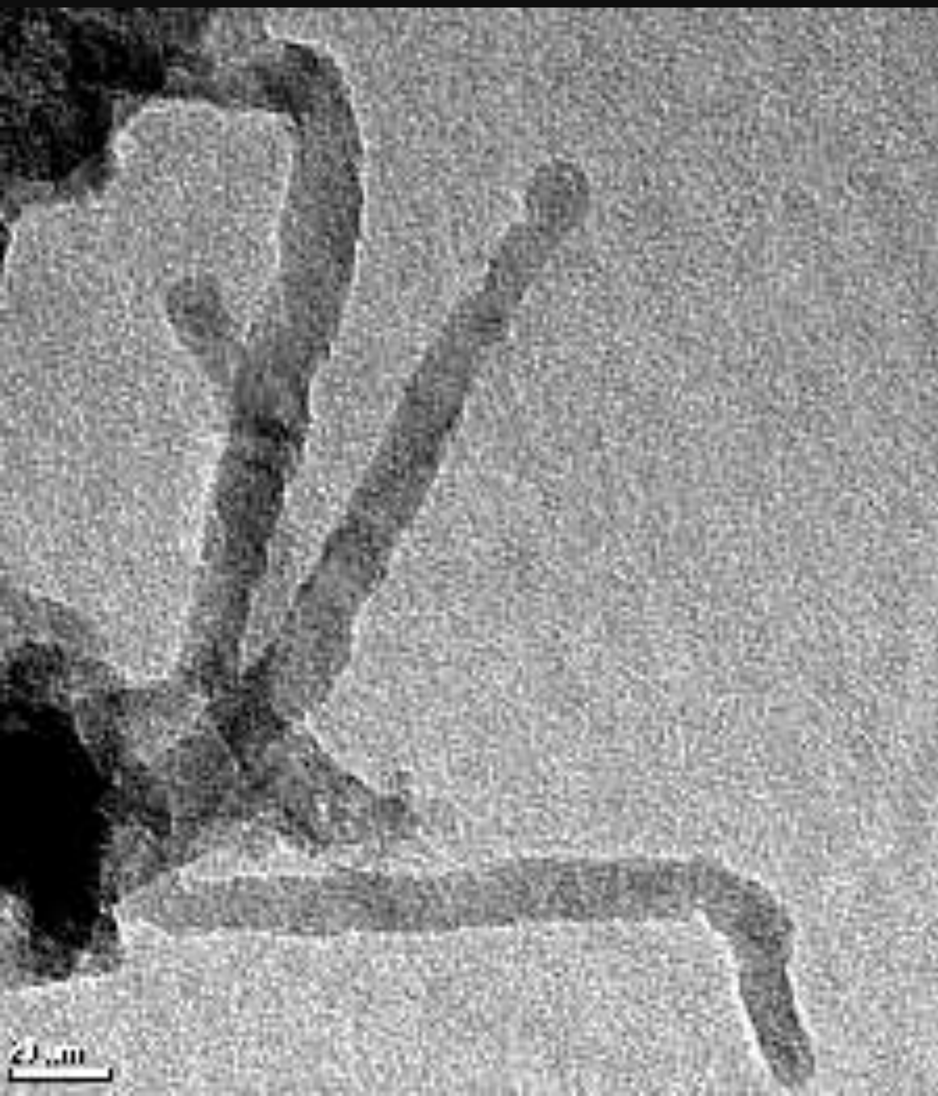
- Nanoparticles
- Nanocapsules
- Nanofibers
- Nanowires
- Fullerenes (carbon 60)
- Nanotubes
- Nanosprings
- Nanobelts
- Quantum dots
- Nanofluidies

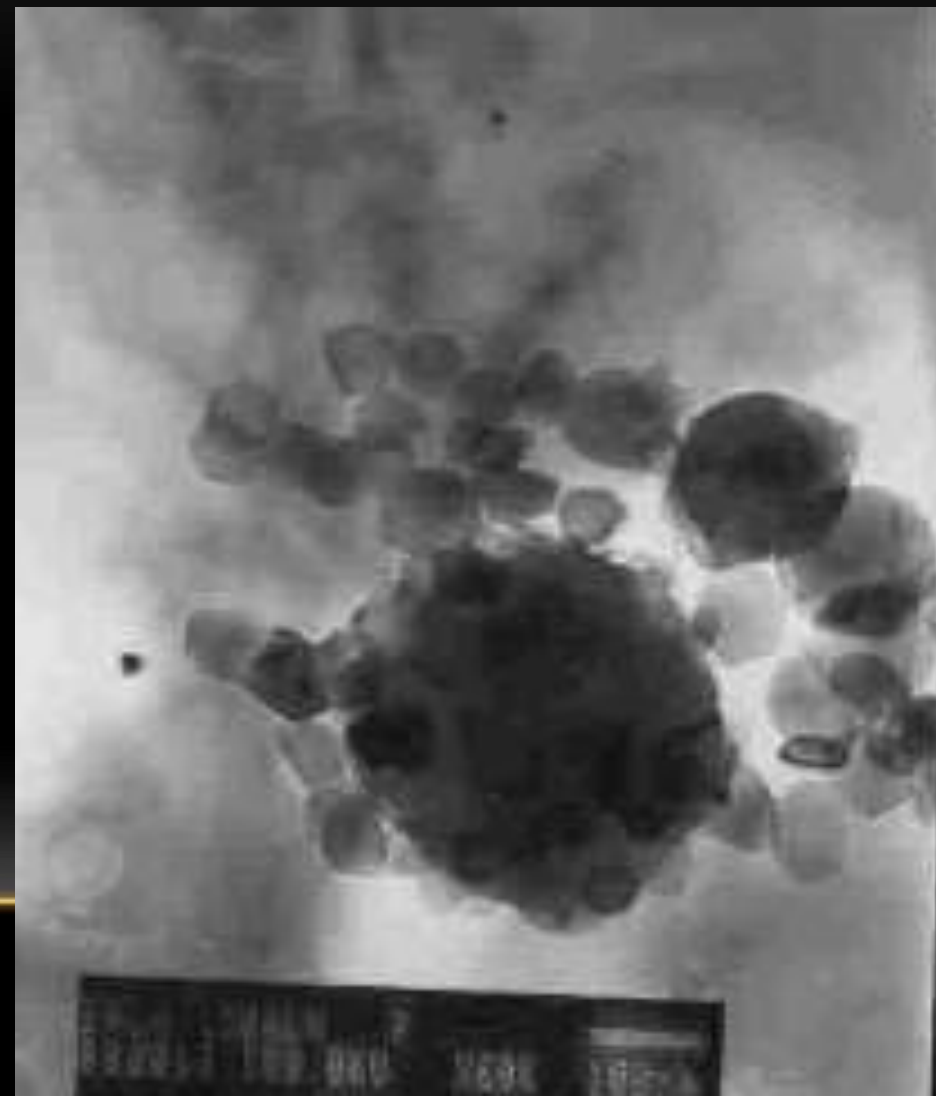
- Nanoparticles (NPs), due to the unique properties afforded by their size, possess a wide range of applications in the industrial, electrical, agricultural, pharmaceutical, and medical fields.
- One-dimensional nanostructures have numerous applications in science and technology due to their fascinating electrical, optical and thermal properties.
- The unique properties of nanometer-scale particles can be utilized in a broad range of fields from catalyst to optical filters or nanolithography.
- Small particles differ from the bulk materials due to surface shape and quantum size effects.
- IR spectroscopy gives an insight into the molecular structure through the specific vibrational frequencies.
- The absorption of IR is characteristic for the chemical composition and structure of materials. It can be considered as a material's "fingerprint".

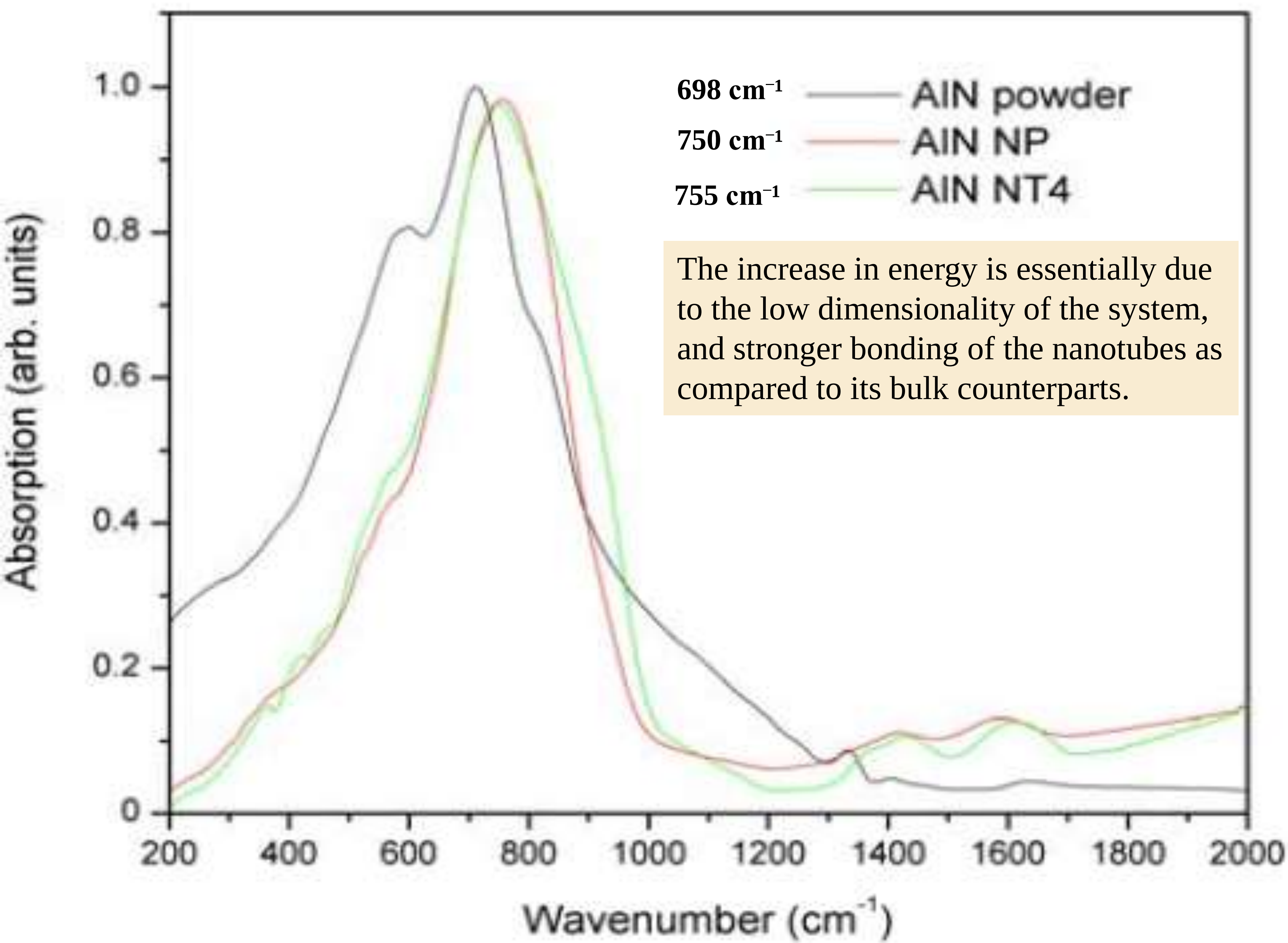
Aluminium nitride nano-systems

- Aluminium nitride (AlN) is a wide band-gap semiconductor and has properties similar to that of diamond.
- AlN crystallizes in the hexagonal wurtzite and cubic zincblend phase.
- Both aluminium nitride nanoparticles (NP) and nanotubes (NT) were synthesized.
- The main infrared active phonons of the Al-N bonds occur in the domain 200-1000 cm^{-1}.

- Definite and systematic shifts in the absorption values for both nanotubes and nano-particles as compared with the bulk spectra.



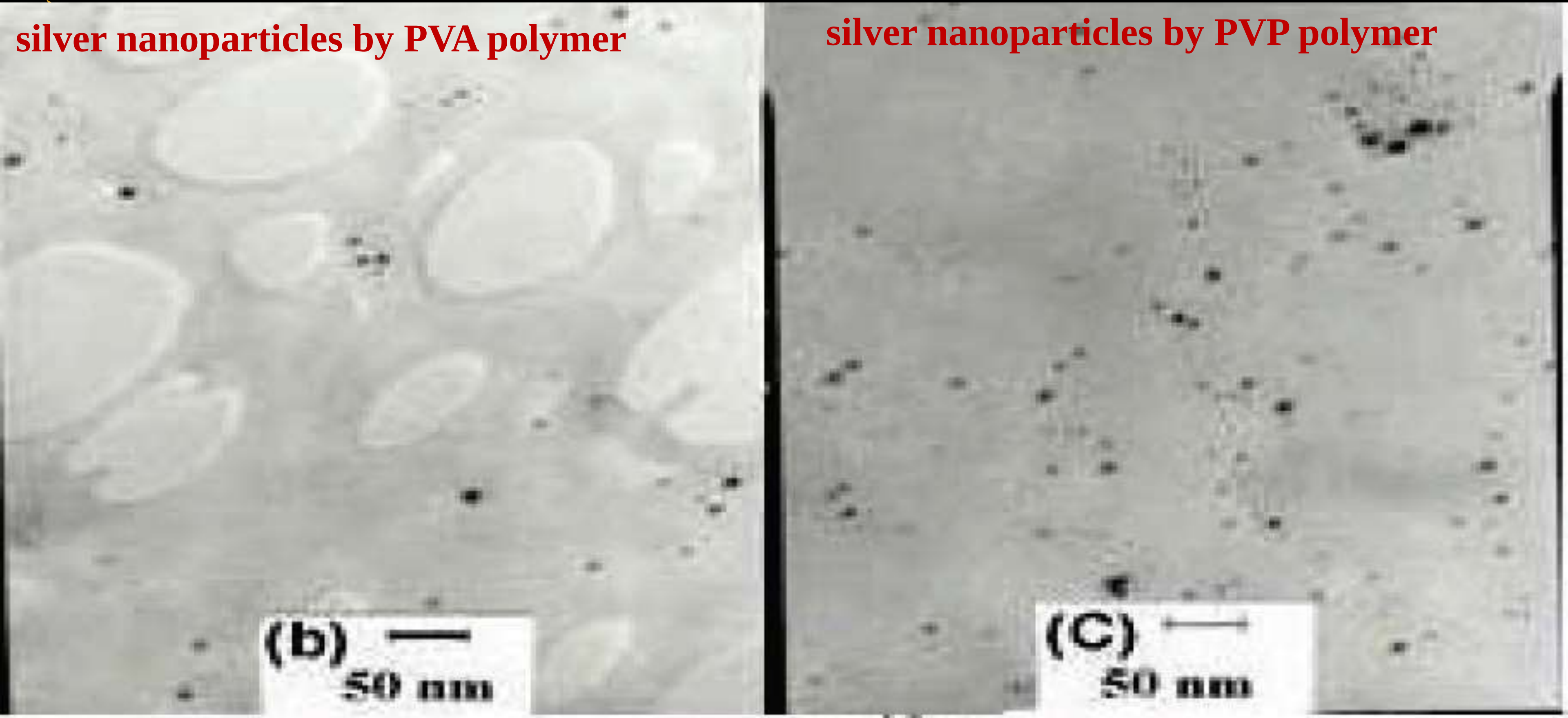


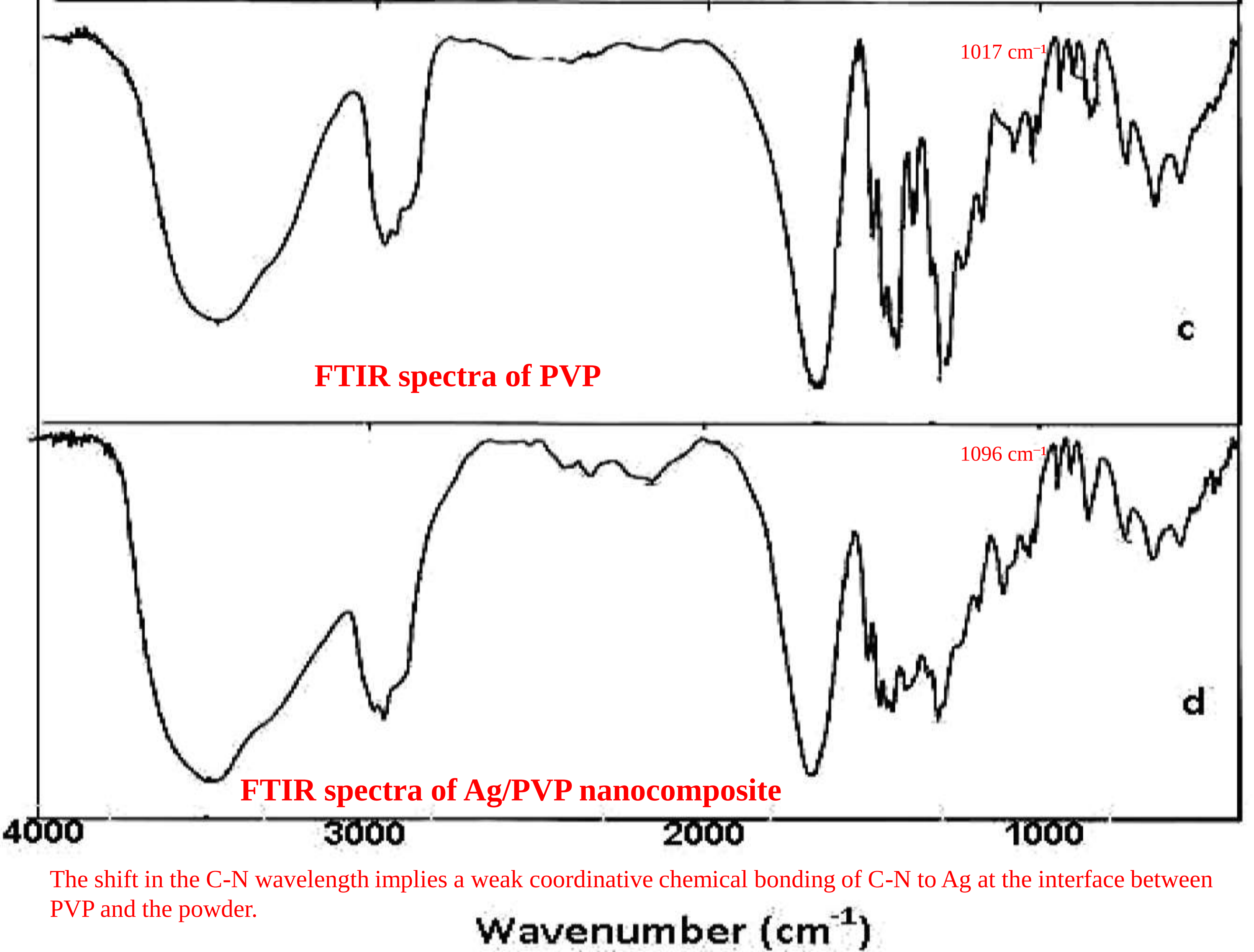


The increase in energy is essentially due to the low dimensionality of the system, and stronger bonding of the nanotubes as compared to its bulk counterparts.

Silver Nanoparticles

- Monodisperse inorganic nanoparticles have practical applications ranging from biosensing to catalysis, optics, and data storage.

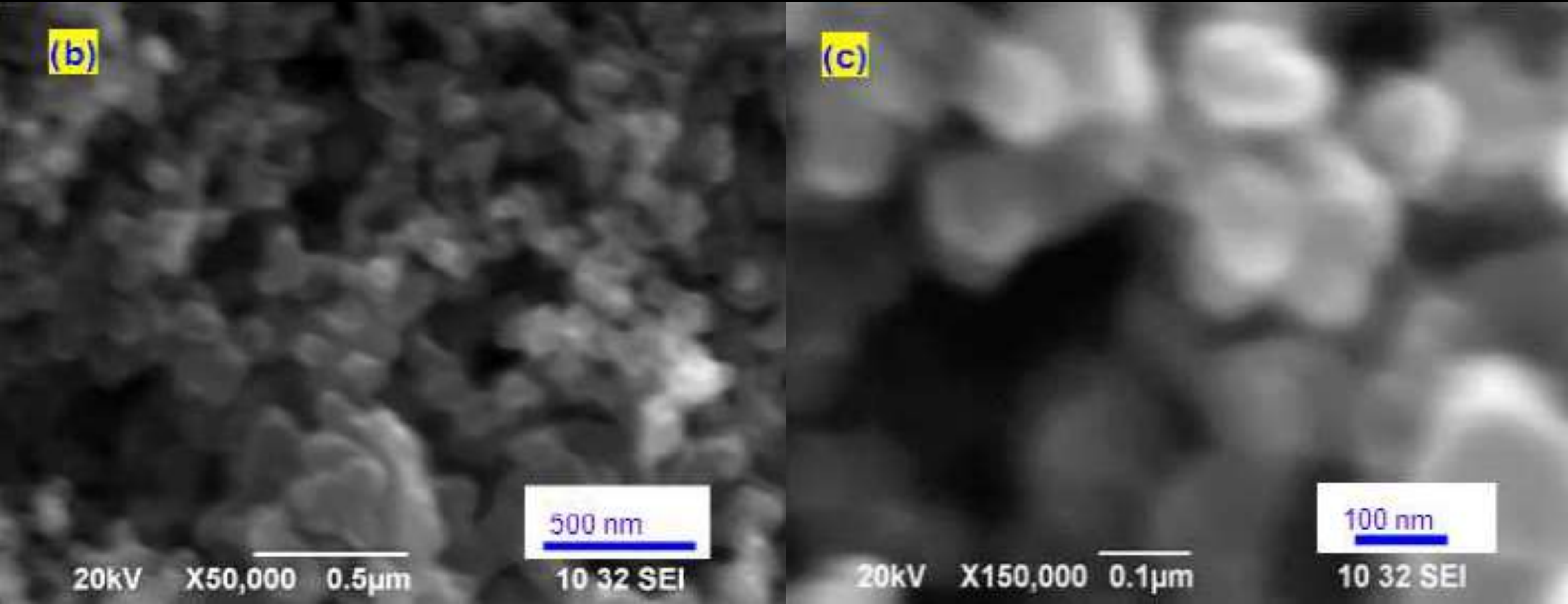


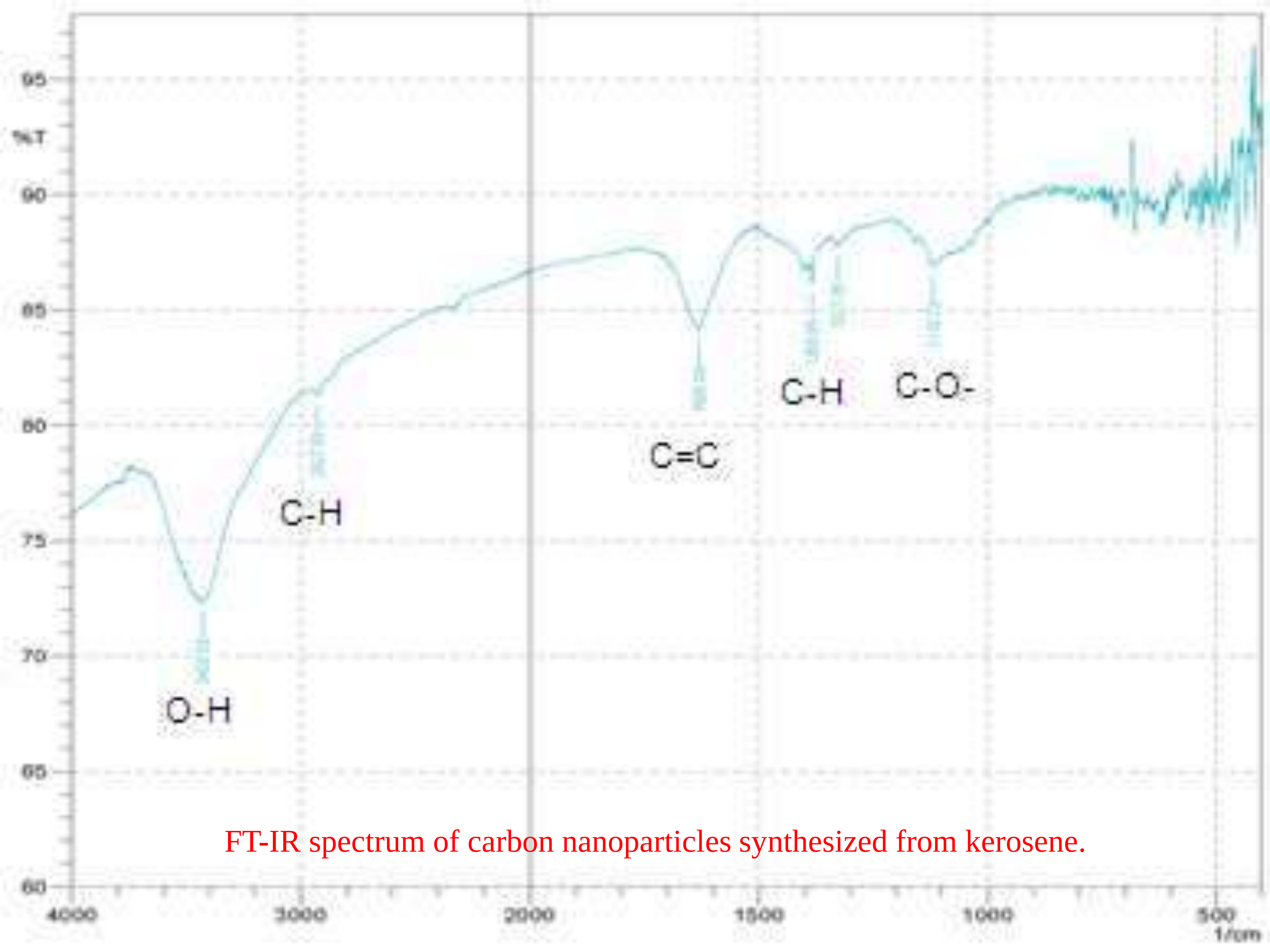


The shift in the C-N wavelength implies a weak coordinative chemical bonding of C-N to Ag at the interface between PVP and the powder.

Carbon nanoparticles

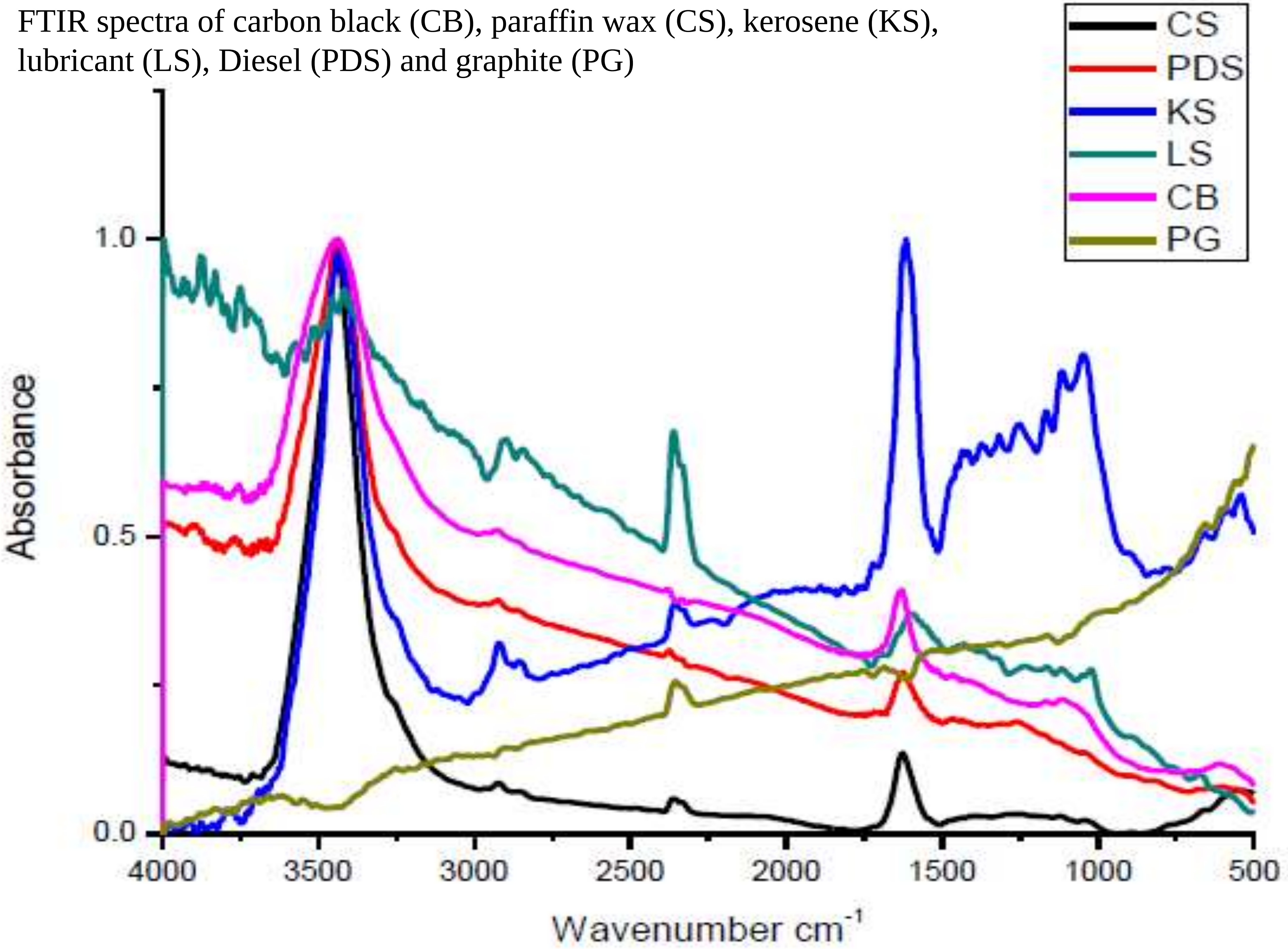
- Carbon sources for the synthesis of pure and inexpensive carbon nanoparticles.
- Combustion reactions come to equilibrium, and only carbon materials can be deposited on the surface of glass plate which characterized by FTIR analysis.





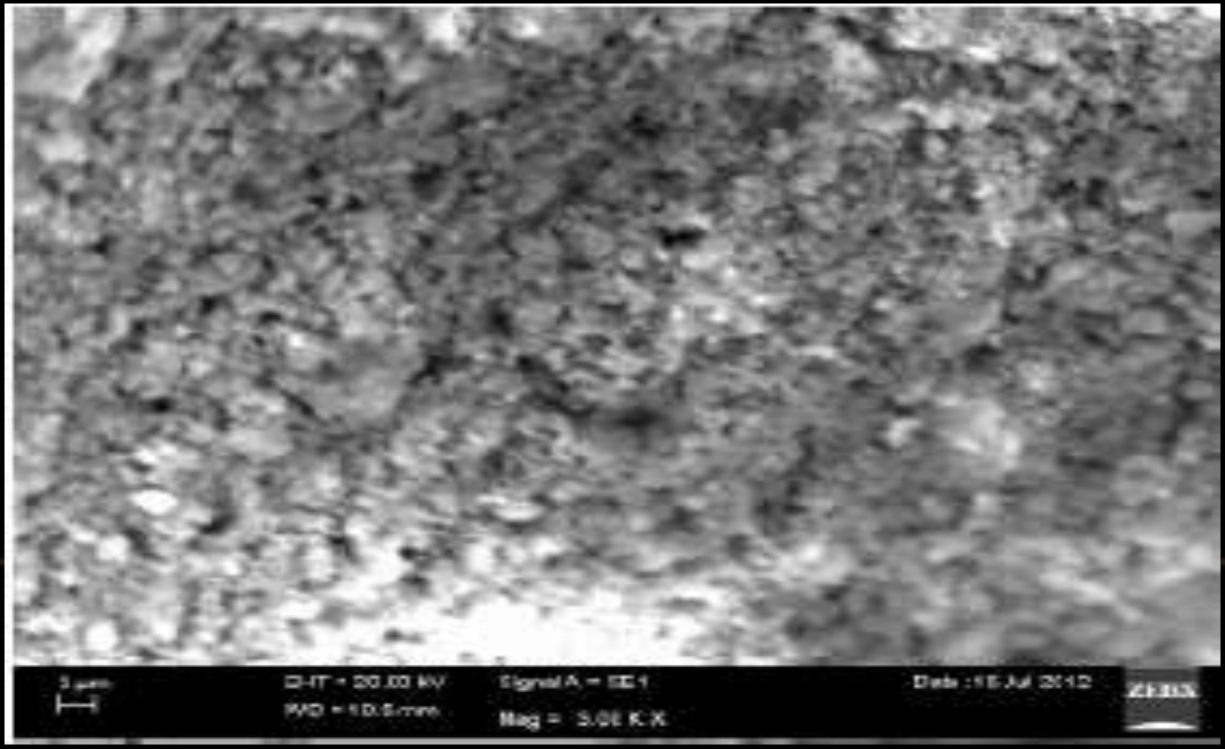
FT-IR spectrum of carbon nanoparticles synthesized from kerosene.

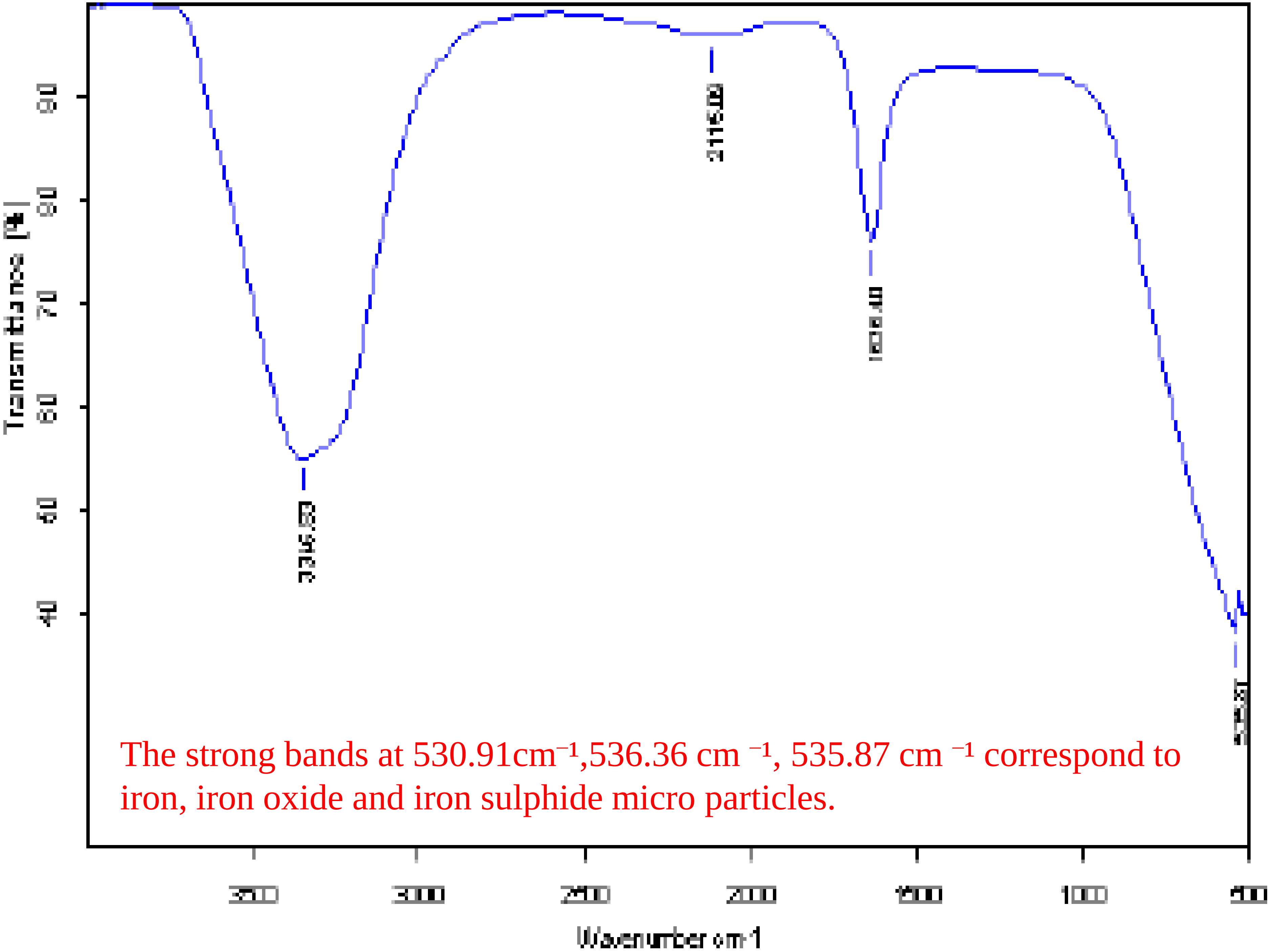
FTIR spectra of carbon black (CB), paraffin wax (CS), kerosene (KS), lubricant (LS), Diesel (PDS) and graphite (PG)



Iron Based Micro and Nanoparticles

- Iron plays an important role in contaminant mobility, sorption and breakdown due to its role as an electron donor (**Fe^{+2} to Fe^{+3}**)
- Iron able to co-ordinate to Oxygen, Nitrogen and Sulphur atoms and to bind additional small molecules.
- Iron plays an important role in many reactions in the human body.



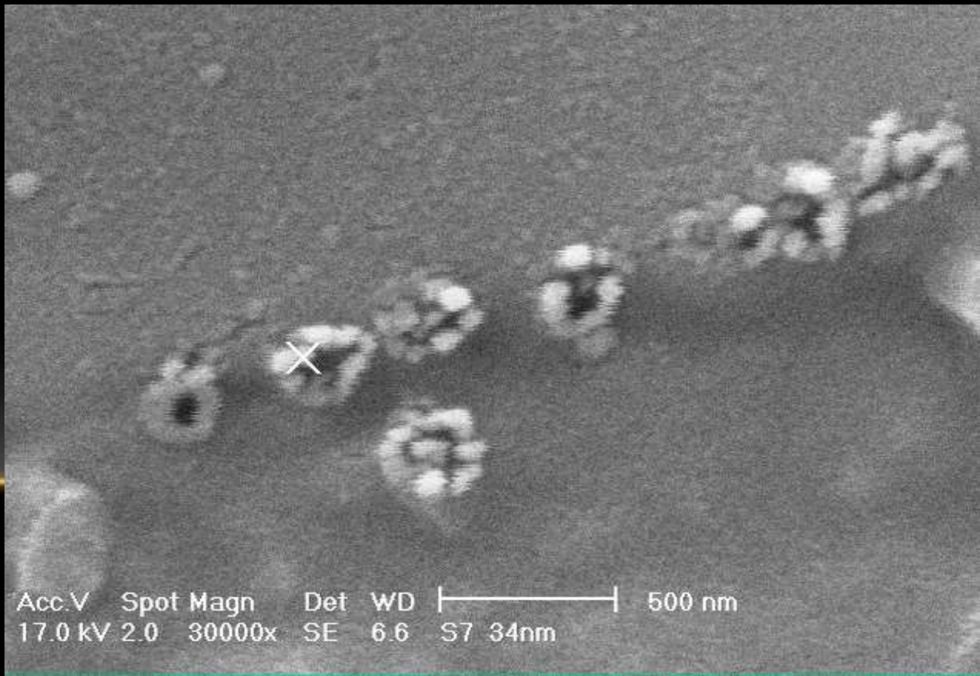


The strong bands at 530.91cm^{-1},536.36 cm $^{-1}$, 535.87 cm $^{-1}$ correspond to iron, iron oxide and iron sulphide micro particles.

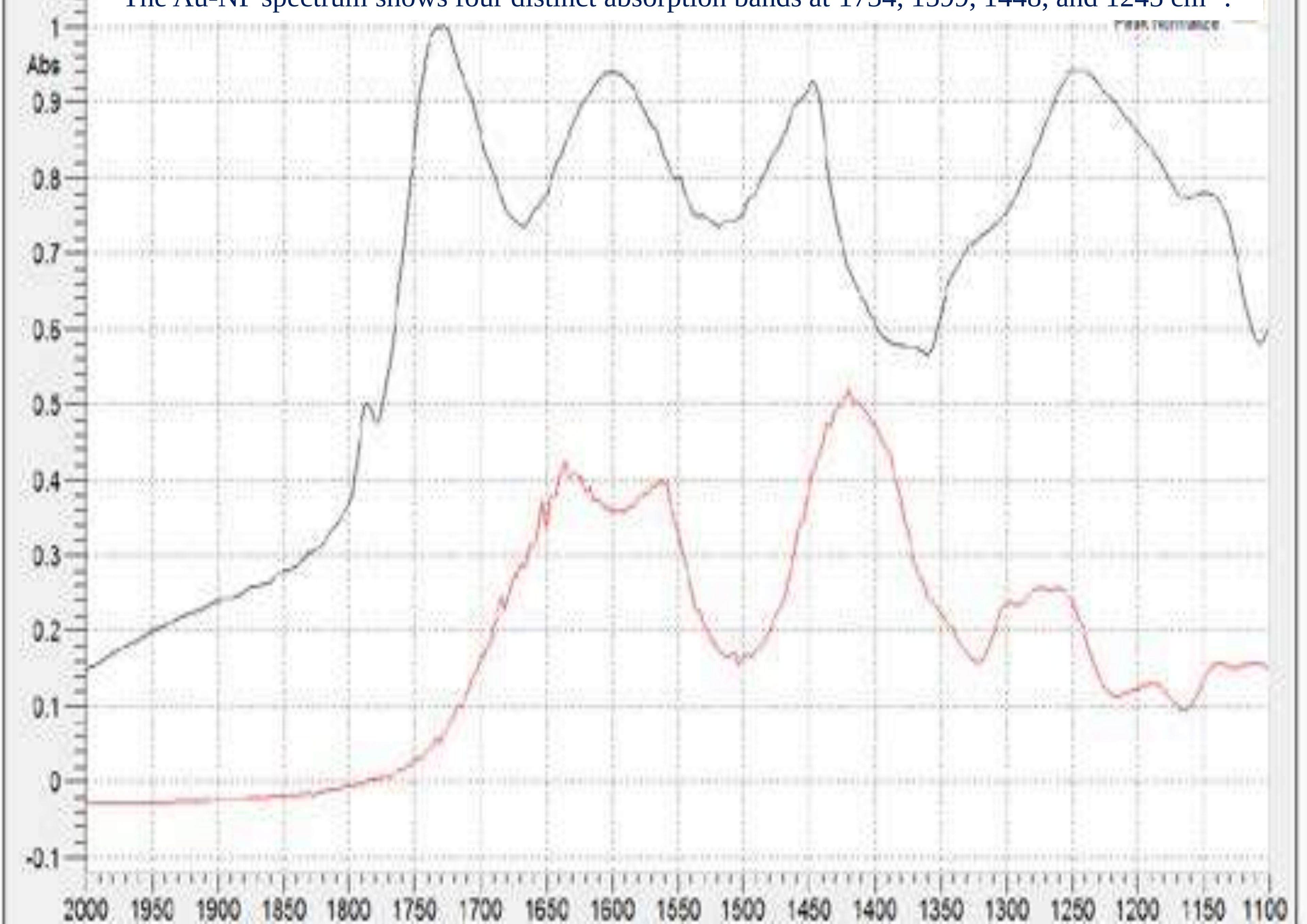
Gold Nanoparticle

- ✓ Gold is a rare element which has been used to treat different diseases such as cancer diagnostics and therapy.
- ✓ Gold nanoparticles (Au-NPs) have been used as anti-HIV, antiangiogenesis, anti-malarial and anti-arthritic agent.
- Au-NPs make them very promising for specific applications such as medical imaging, drug delivery, gene delivery, and molecular sensing.

Trop J Pharm Res, December 2012;11 (6): 887



The Au-NP spectrum shows four distinct absorption bands at 1734, 1599, 1448, and 1245 cm⁻¹.



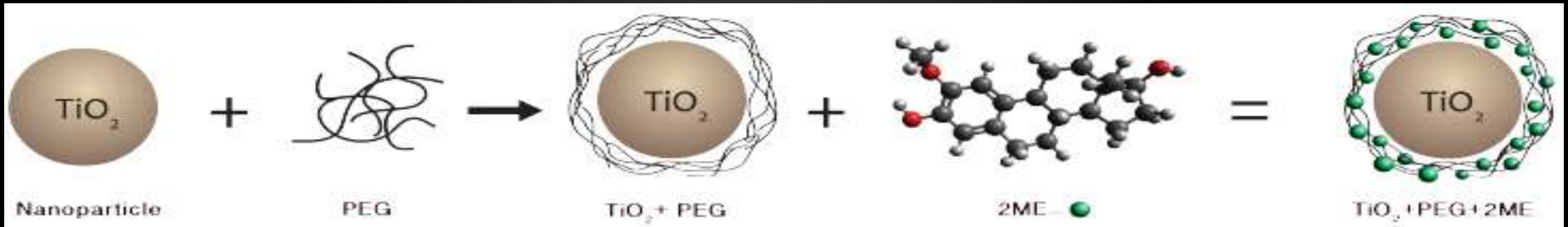
TiO_2 Nanoparticles

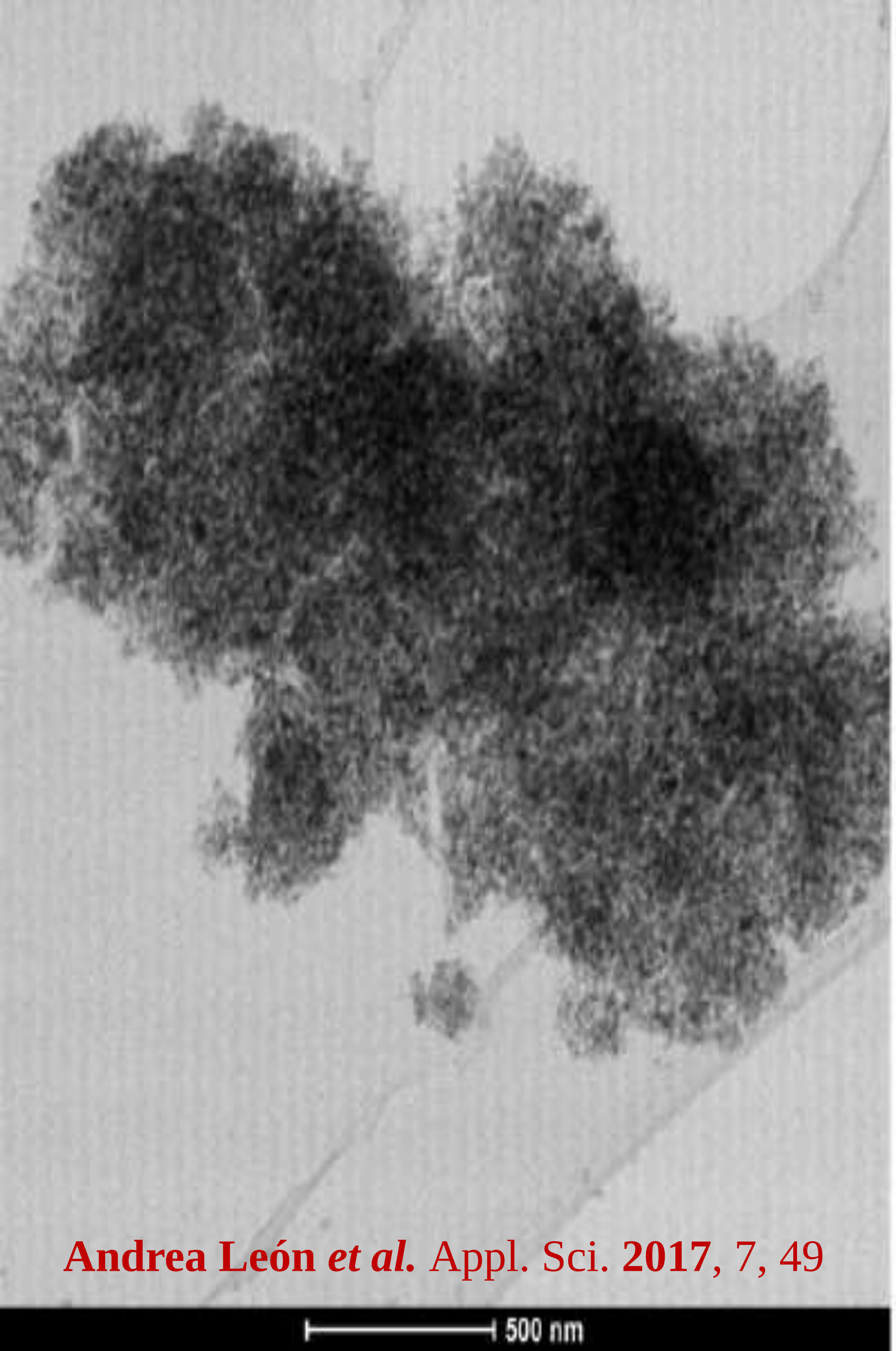
- Titanium dioxide (TiO_2) is considered to be a potential semiconductor for biocidal applications due to its photocatalytic properties, which explain its ability to destroy bacteria, viruses, and even cancer cells.

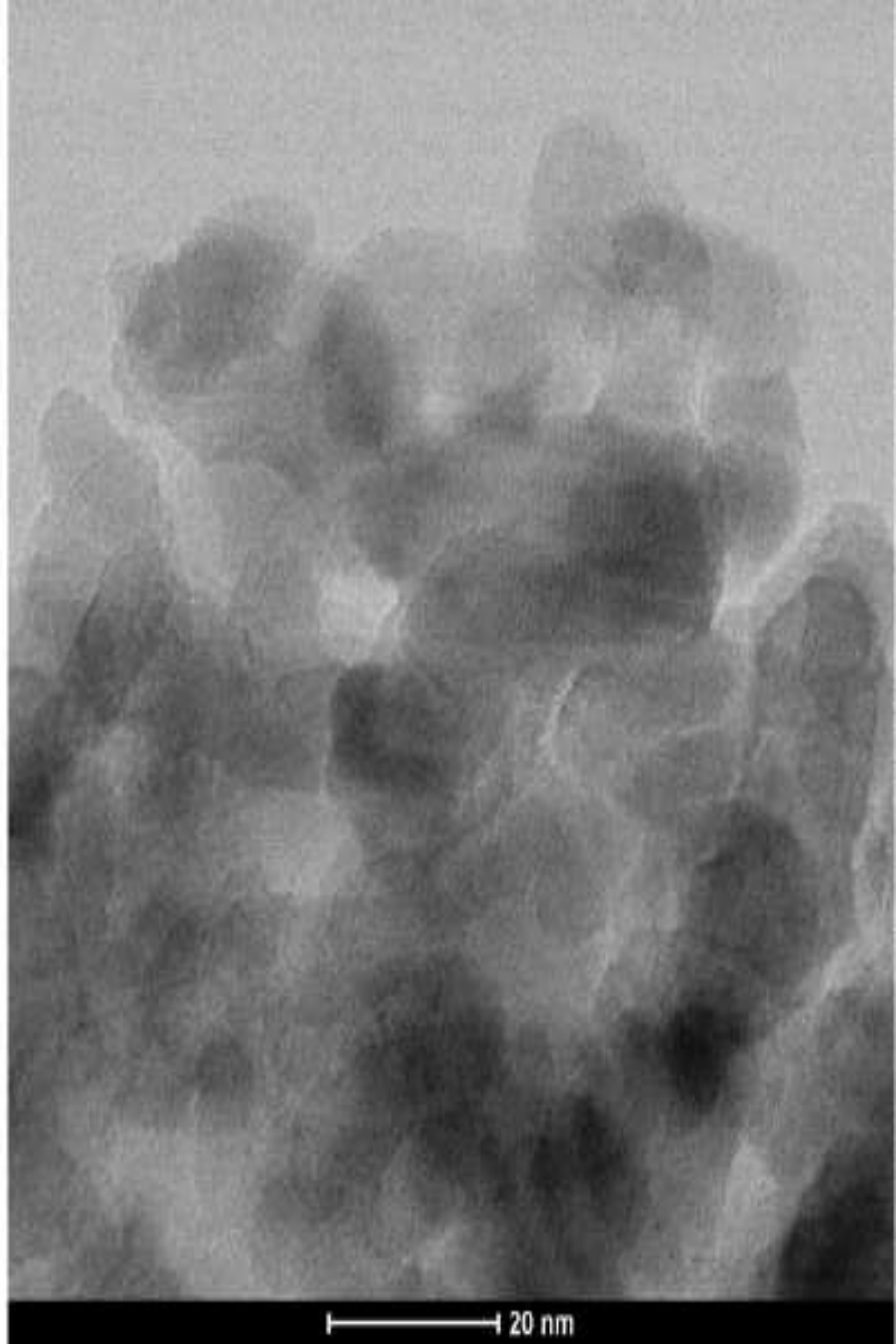
- TiO_2 NPs have considerable potential in biomedicines, and a variety of works have been conducted to develop new antibacterial and drug delivery systems based on this nanoparticle.

- TiO_2 has been classified as a biologically inert substance in animals and humans, and it has good biocompatibility and no toxicity in vitro or in vivo.

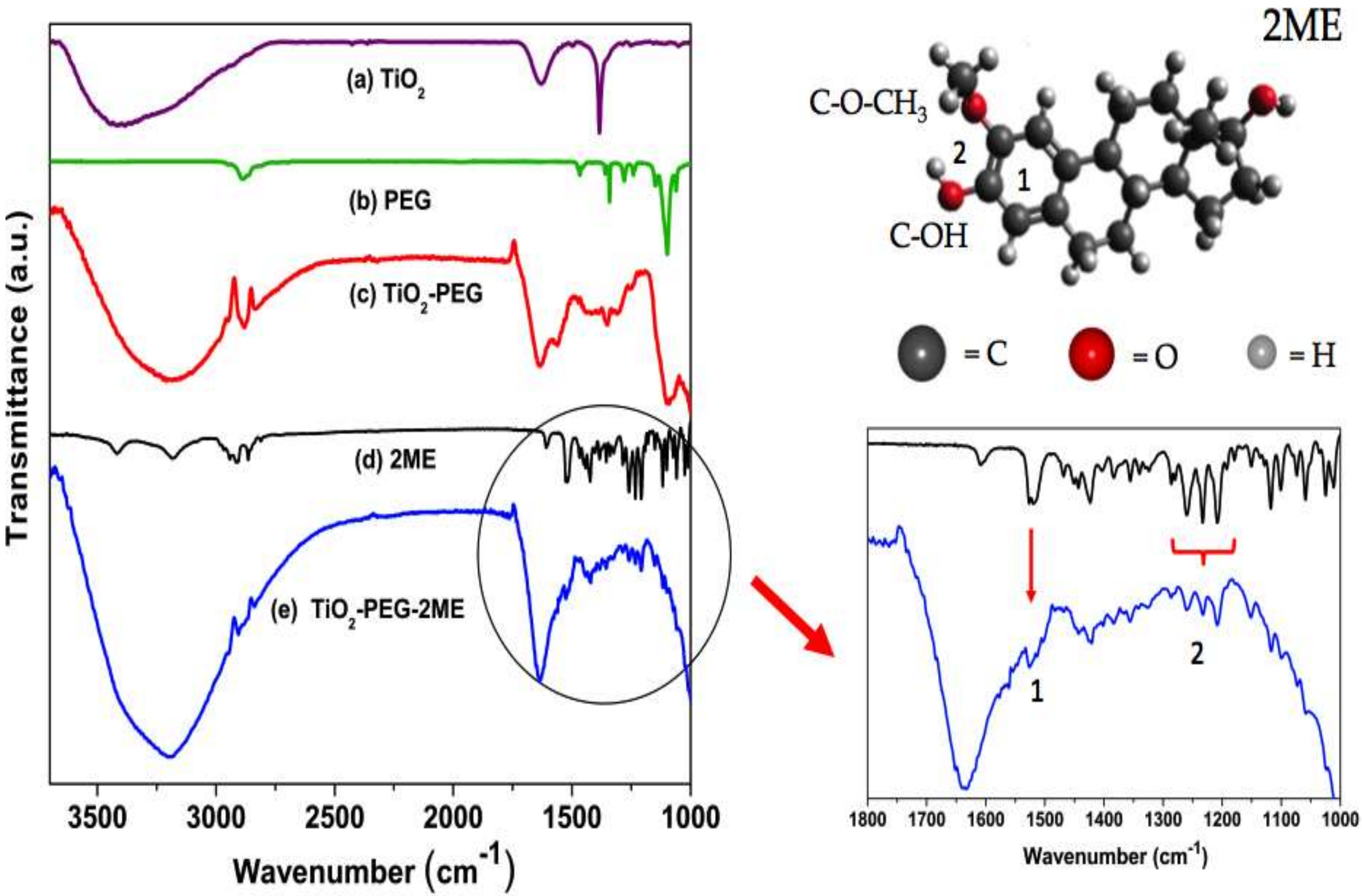
- TiO_2 NPs with polymeric materials to eliminate aggregation and sedimentation, reduce toxicity, and develop biocompatibility.







Andrea León *et al.* Appl. Sci. **2017**, 7, 49

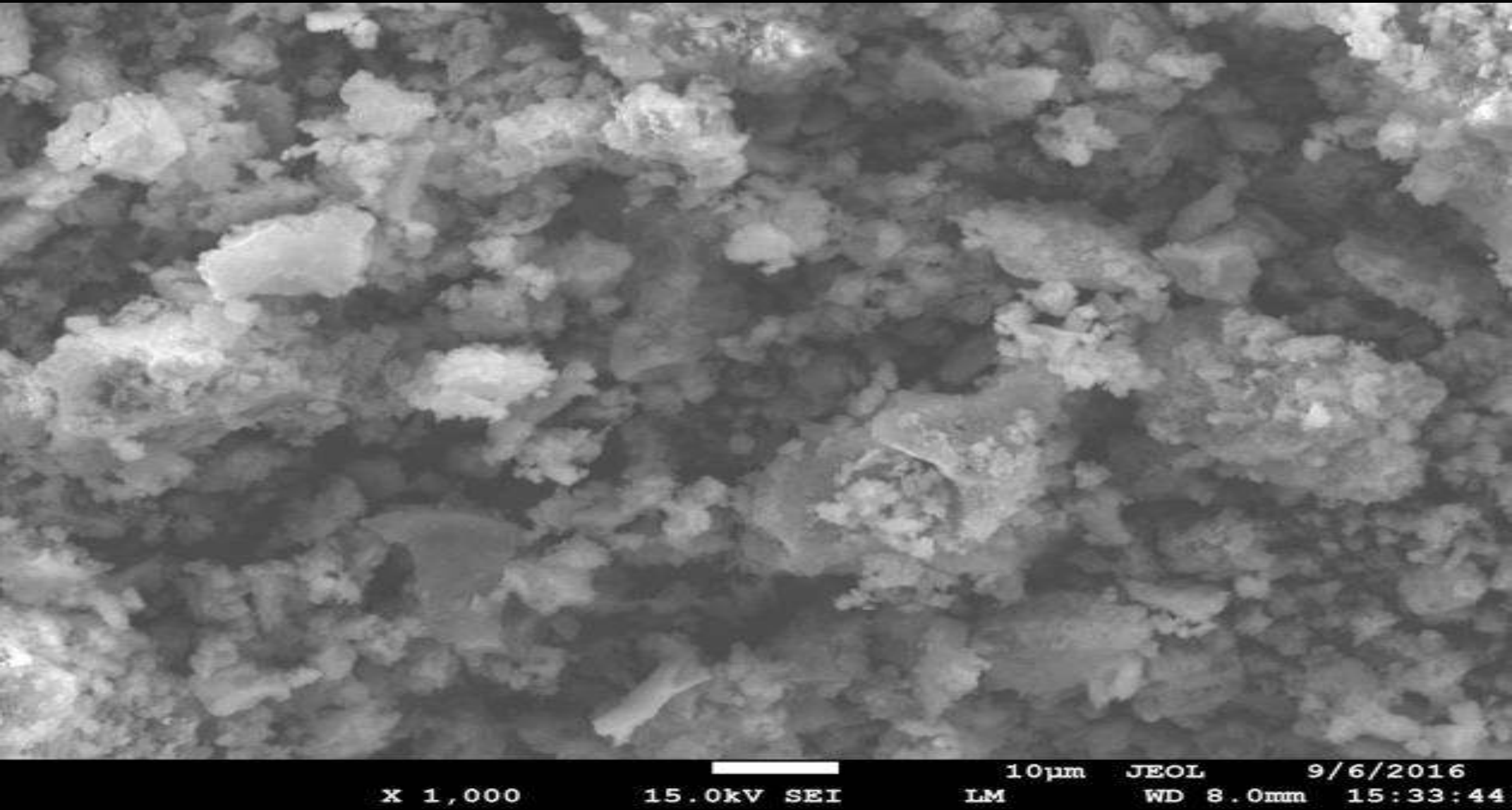


FTIR spectrum of TiO_2 NPs shows, first band at 3500 cm^{-1} (stretching O-H of the TiO_2 NPs), second band 1630 cm^{-1} (bending of Ti-OH), third band at 1383 cm^{-1} (Ti-O modes).

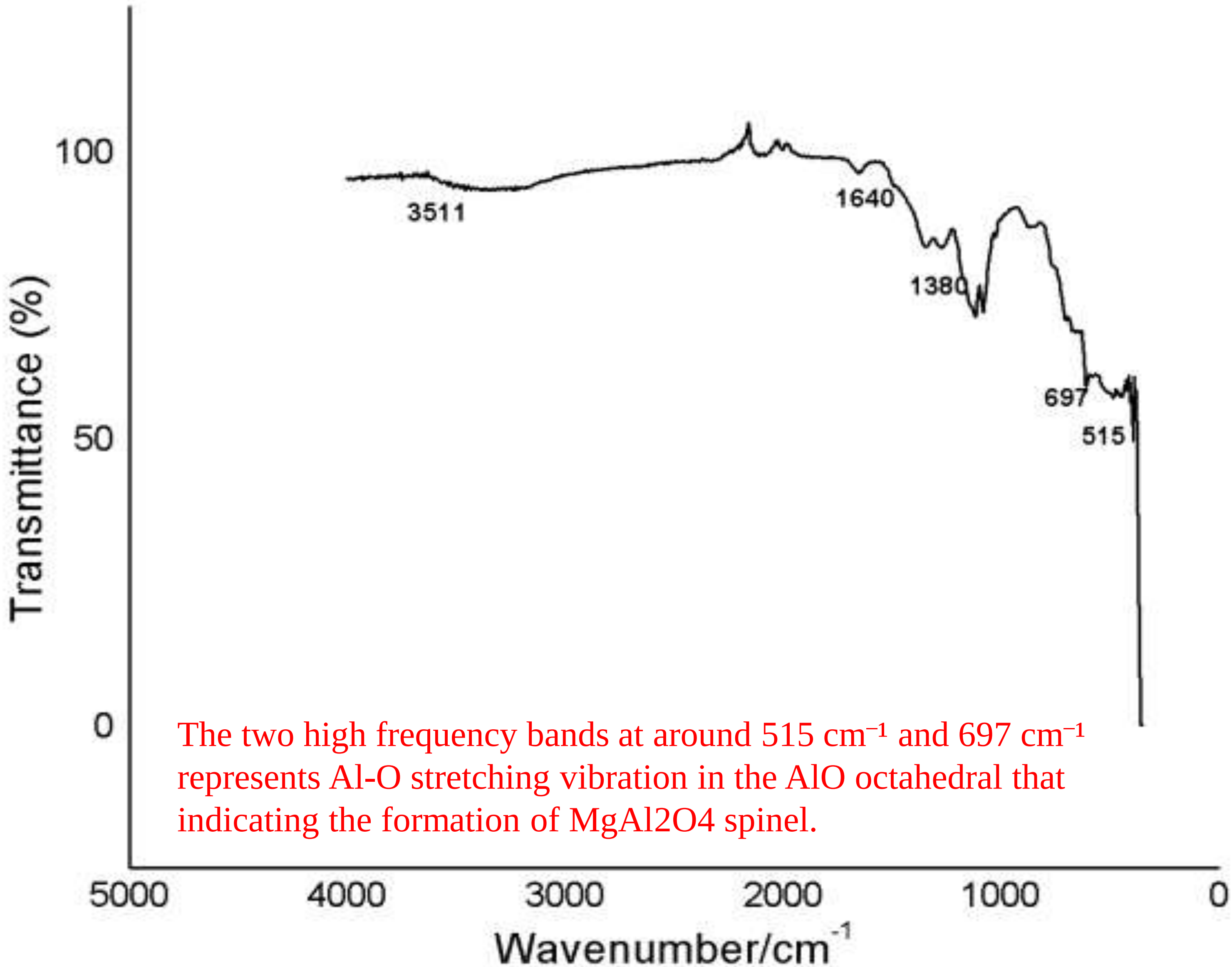
Andrea León *et al.* Appl. Sci. **2017**, 7, 49

$MgA1_2O_4$ NANOPARTICLES

- $MgAl_2O_4$ spinel is of technological interest for its good mechanical and optical properties.



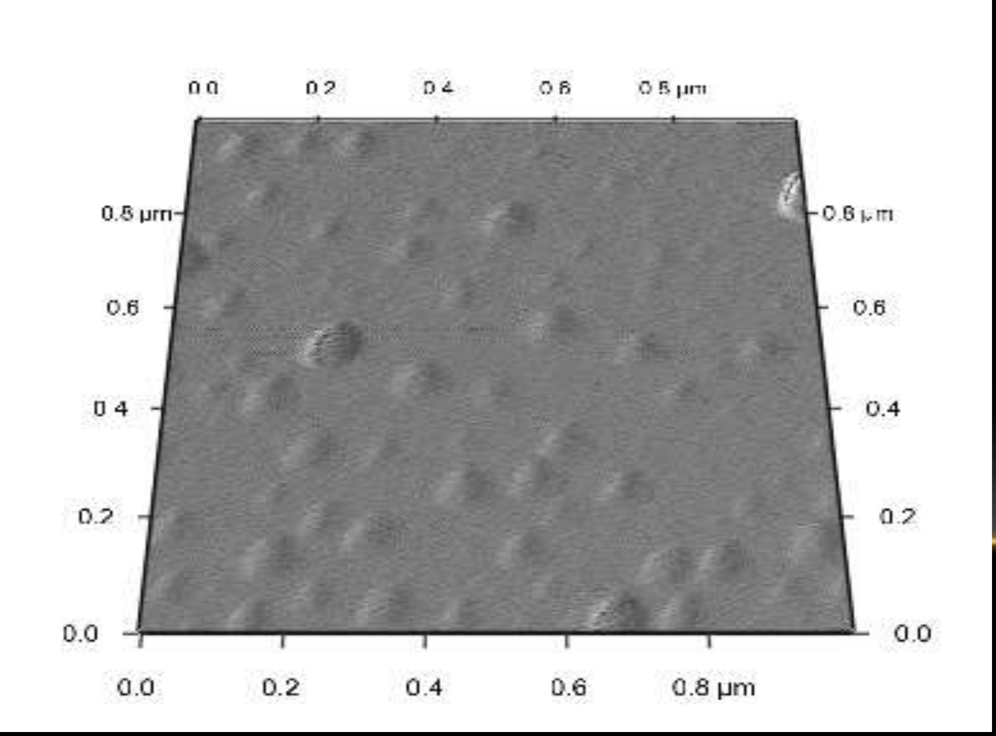
FTIR spectra of $MgAl_2O_4$ nanoparticle

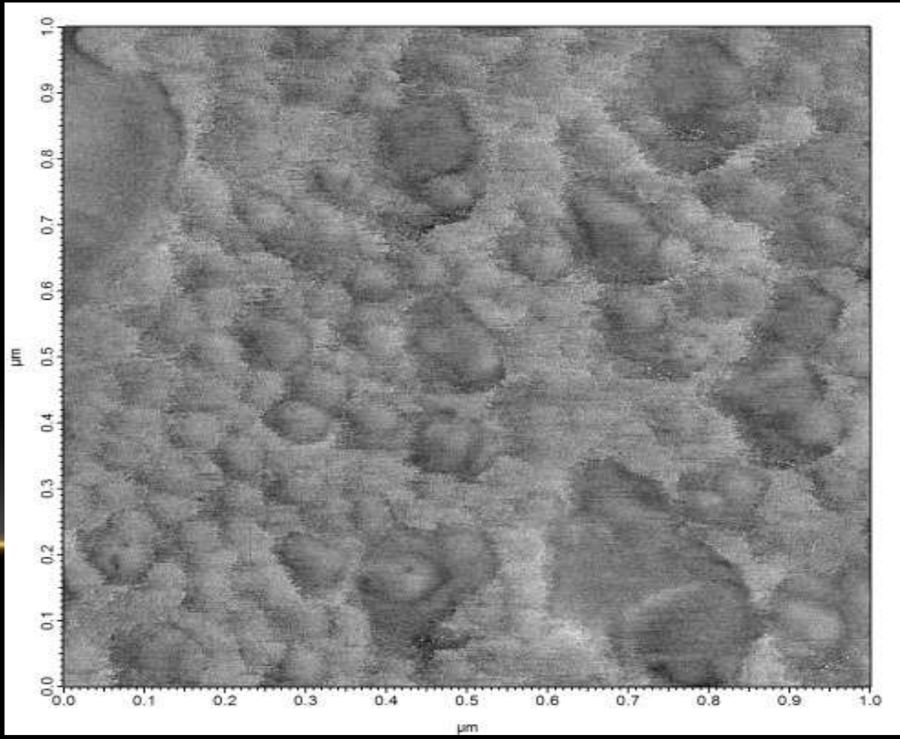


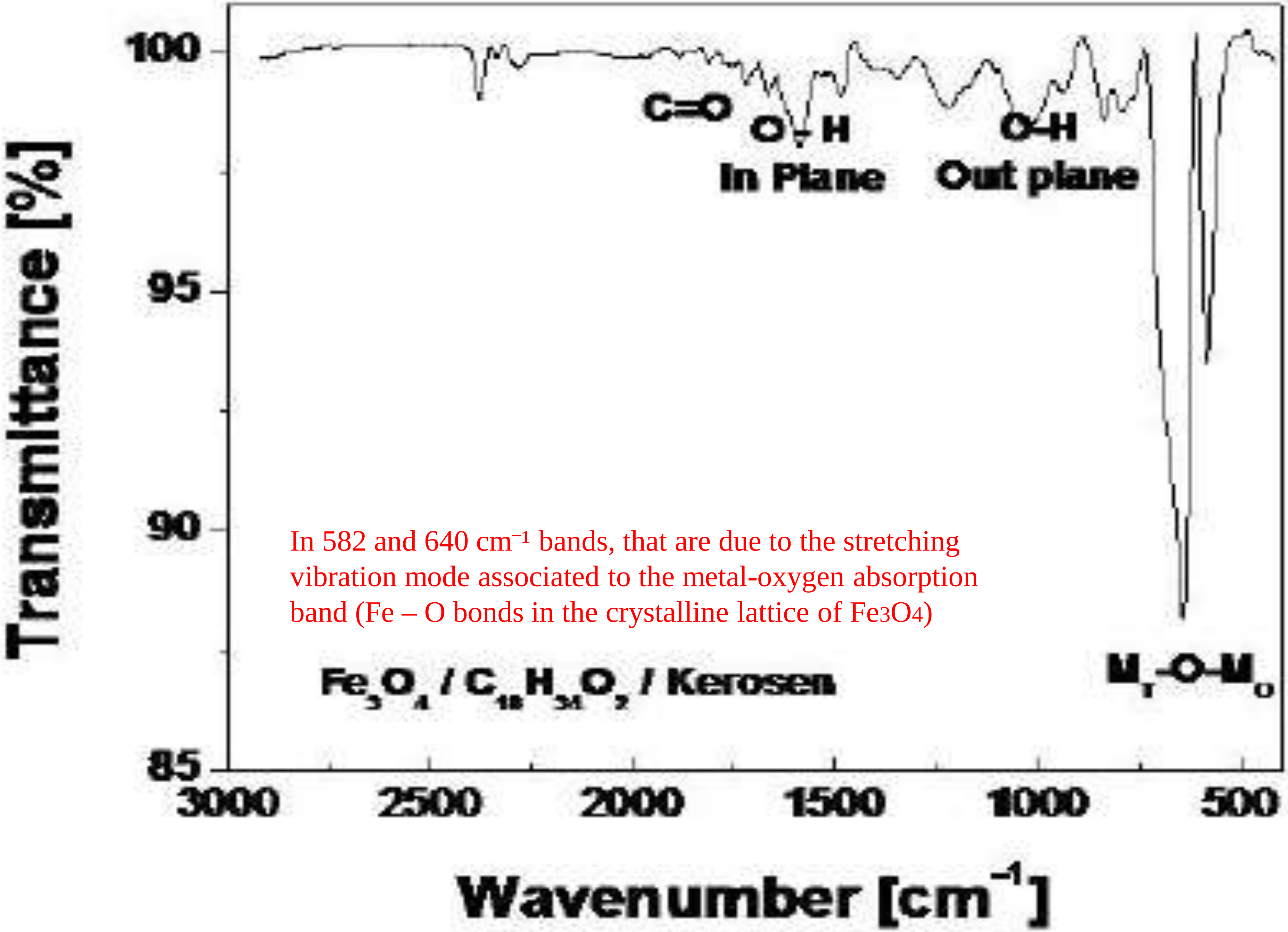
The two high frequency bands at around 515 cm^{-1} and 697 cm^{-1} represents Al-O stretching vibration in the AlO octahedral that indicating the formation of MgAl2O4 spinel.

Fe_3O_4 MAGNETIC NANOFLUID

- Ferrofluids (FF) or magnetic nanofluids are stable magnetic colloids systems composed of nanoparticles of single-magnetic domain with a mean diameter of around 10 nm, dispersed in an organic or inorganic carrier fluids.
- Magnetic nanofluids have been the subject of much interest because of their unusual optical, electronic, and magnetic properties.



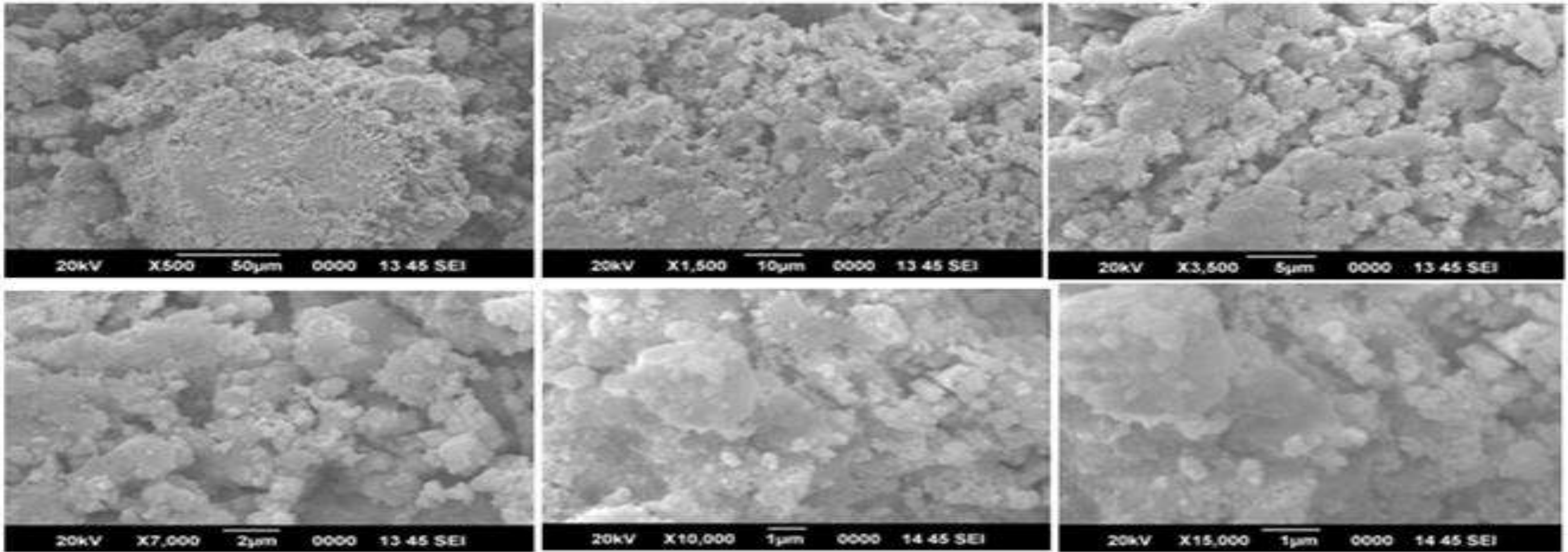


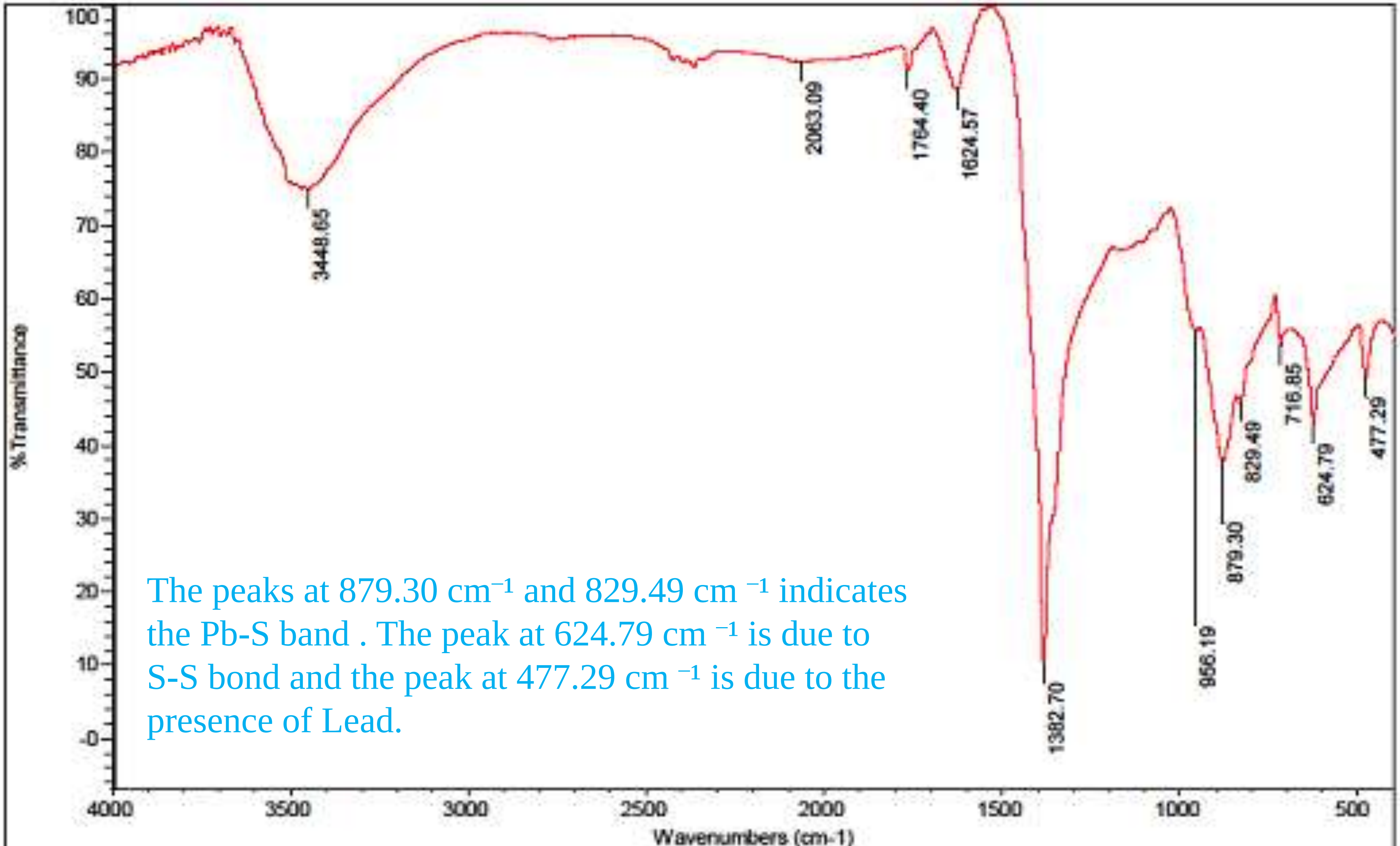


In 582 and 640 cm^{-1} bands, that are due to the stretching vibration mode associated to the metal-oxygen absorption band (Fe – O bonds in the crystalline lattice of Fe_3O_4)

Lead Sulphide Nanoparticles

- Lead sulphide (PbS) is an important semiconductor because of its special small direct-band gap (0.41 eV) and large excitonic Bohr radius of 18 nm.
- The lead sulphide nanoparticles have wide applications in many fields such as solar cells, solar absorbers, photographs, lasers, LED devices, telecommunications, detectors, optical switches, optical amplification, and also as gas - sensing agents.





The peaks at 879.30 cm^{-1} and 829.49 cm^{-1} indicates the Pb-S band . The peak at 624.79 cm^{-1} is due to S-S bond and the peak at 477.29 cm^{-1} is due to the presence of Lead.

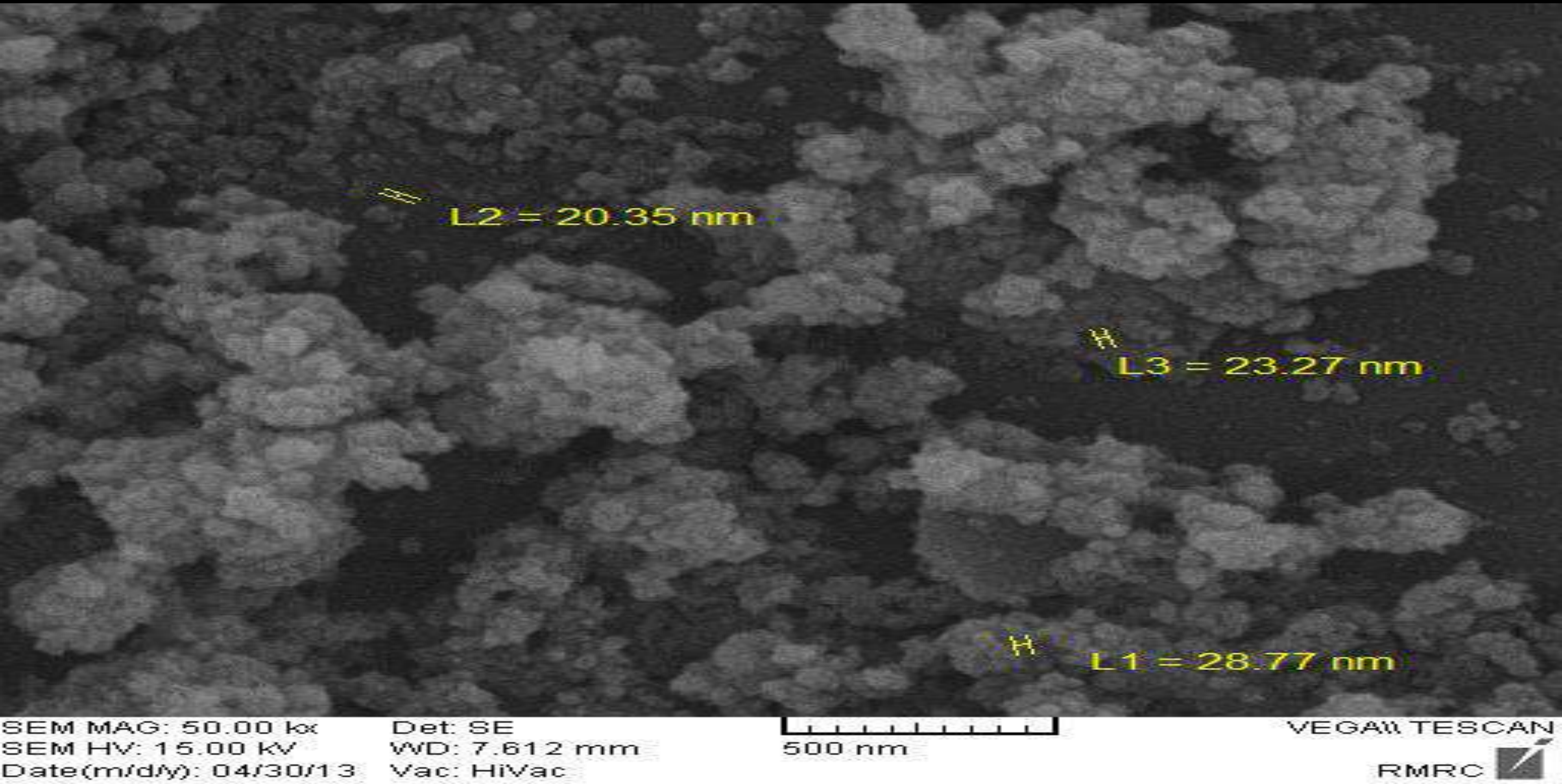
Date: Wed Nov 22 14:23:51 2017 (GMT+05:SAIFFT171115B-01(Lead Sulphide)

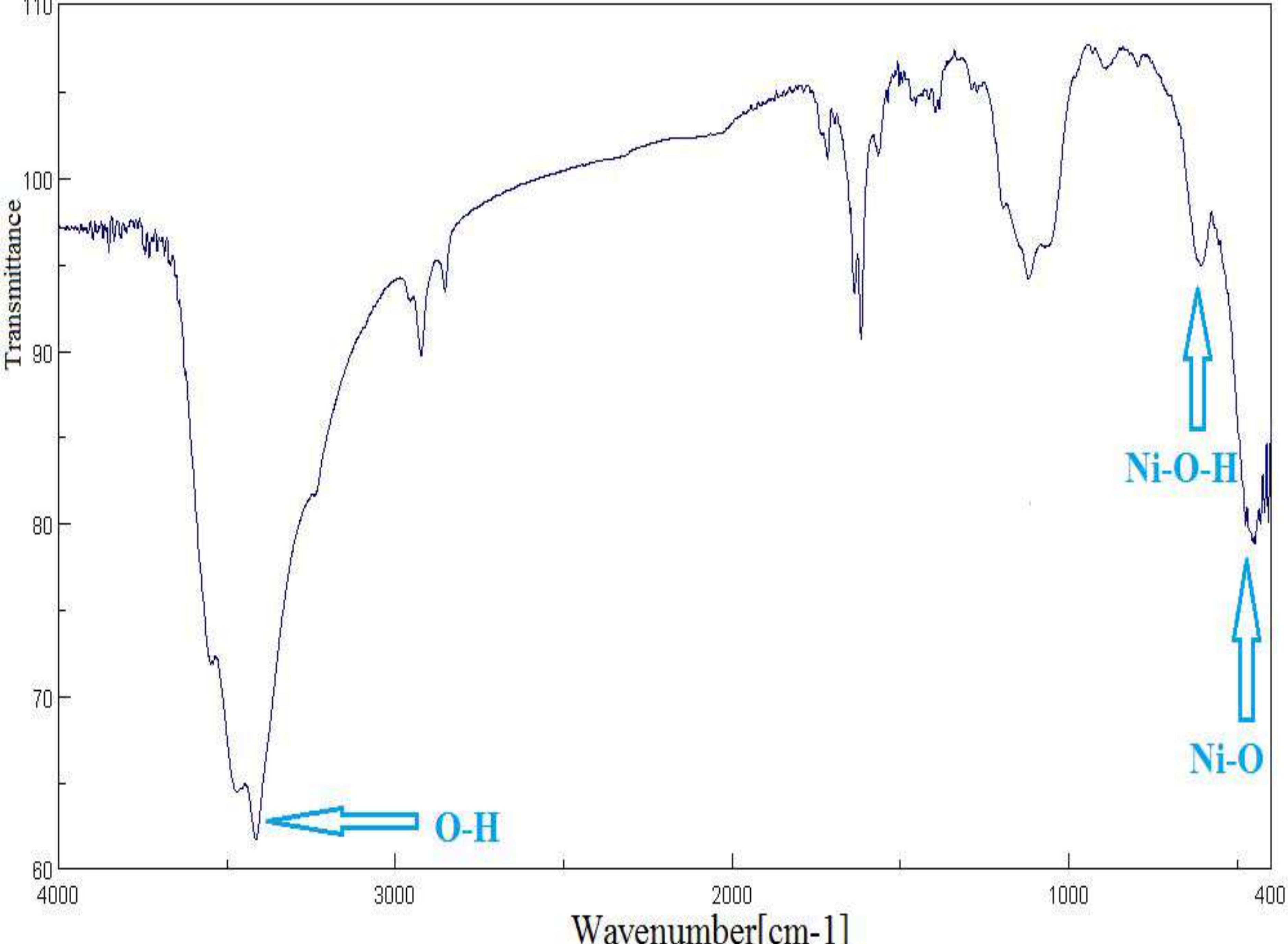
Scans: 32

Resolution: 4.000

Nickl Oxide Nanoparticles

- Nickel oxide (NiO) has considerable attention due to applications, such as catalysts, gas sensors, electrochromic film, fuel cell , magnetic materials , anode of organic light emitting diodes and thermoelectric materials.



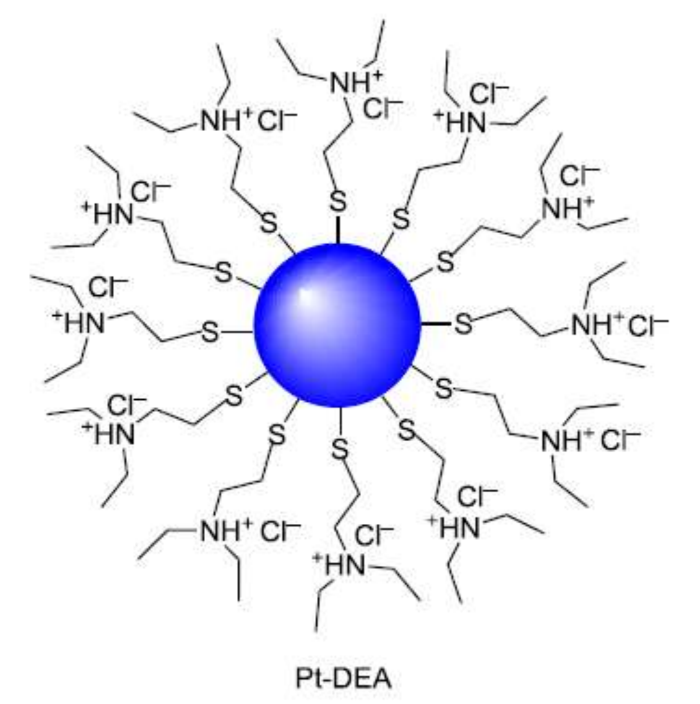


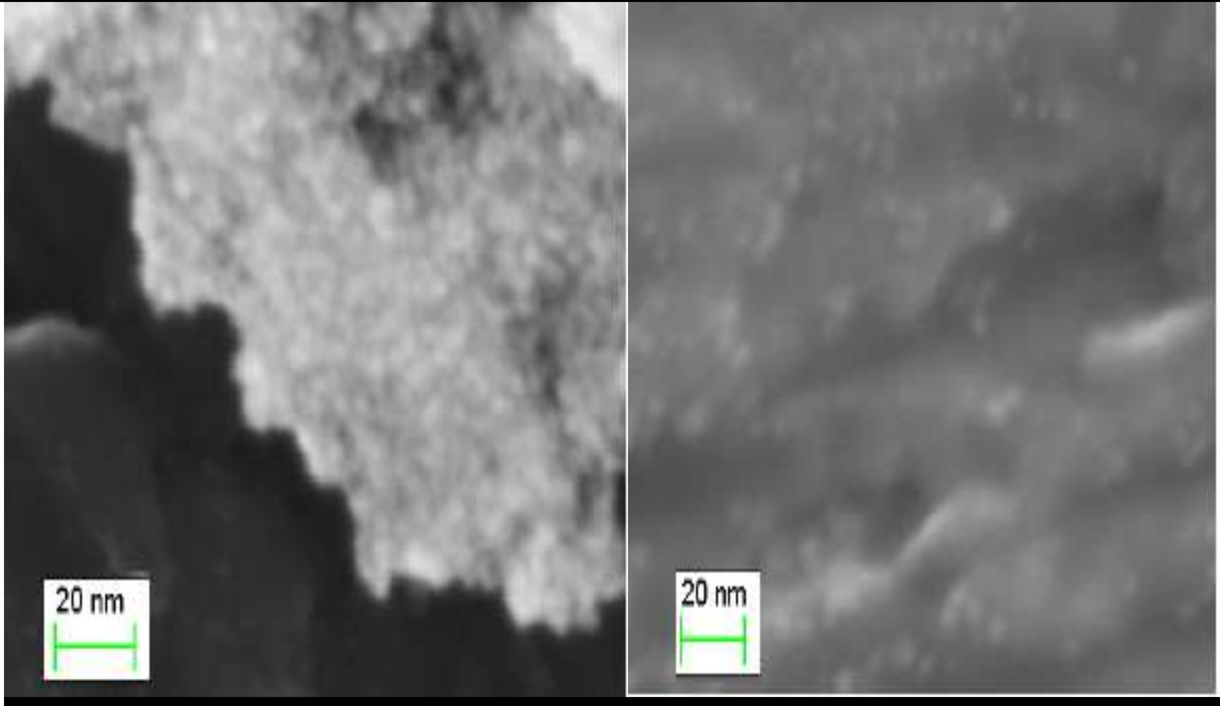
A. Rahdar et al./ JNS 5 (2015) 145-151

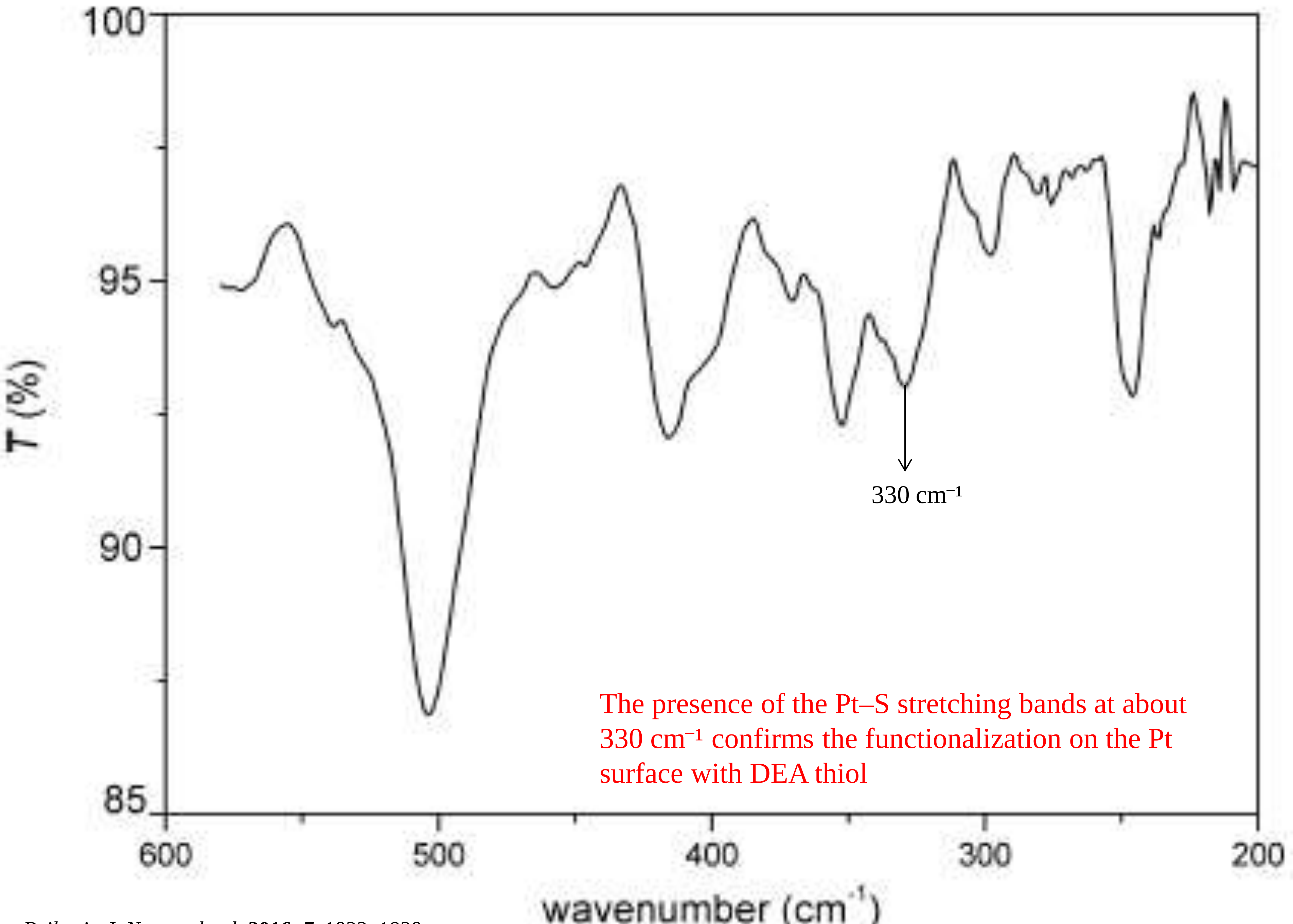
Platinum Nanoparticles

- Platinum nanoparticles (PtNPs) offer a wide range of chemico-physical properties that can be of interest for many technological applications. For example PtNPs are of interest due to their catalytic activity, electrochemical applications, chemical sensing and optical features related to surface plasmon resonance.

- PtNPs were obtained by a wet redox procedure, using 2-diethyl-aminoethanethiol hydrochloride (DEA) as a capping agent.



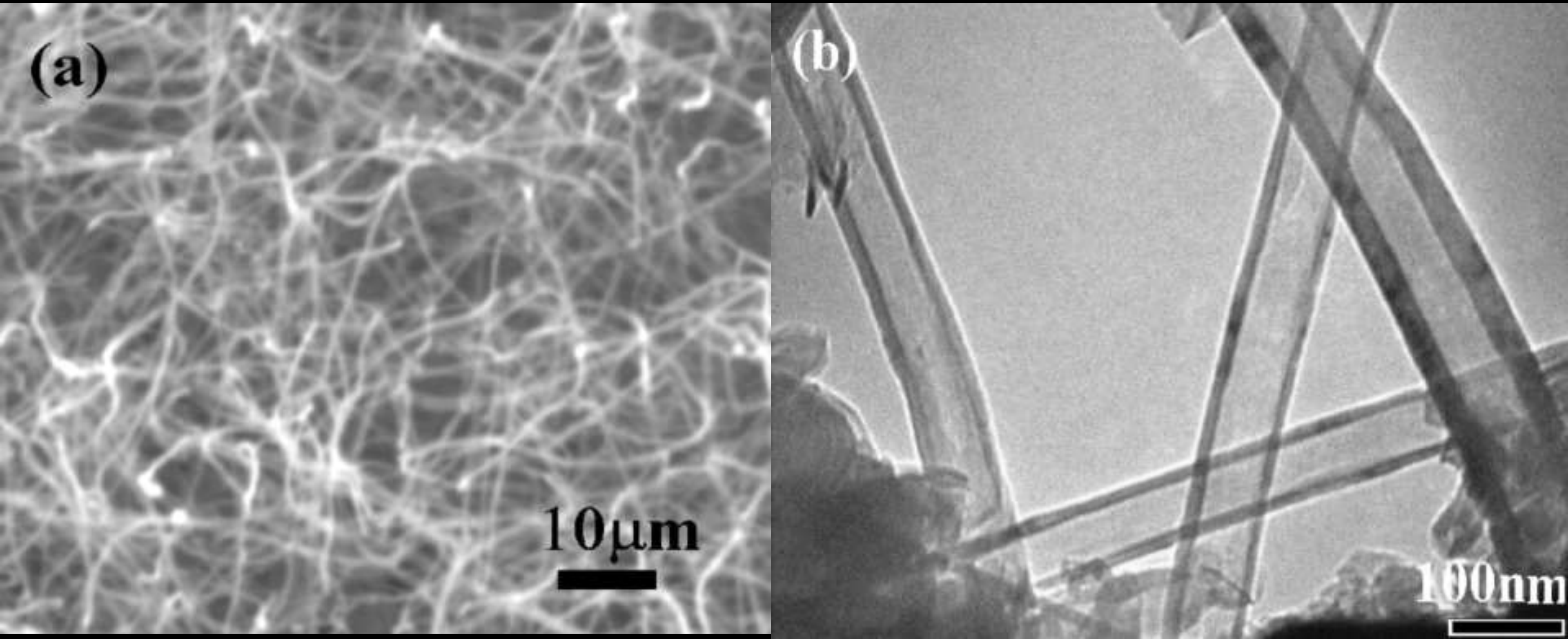


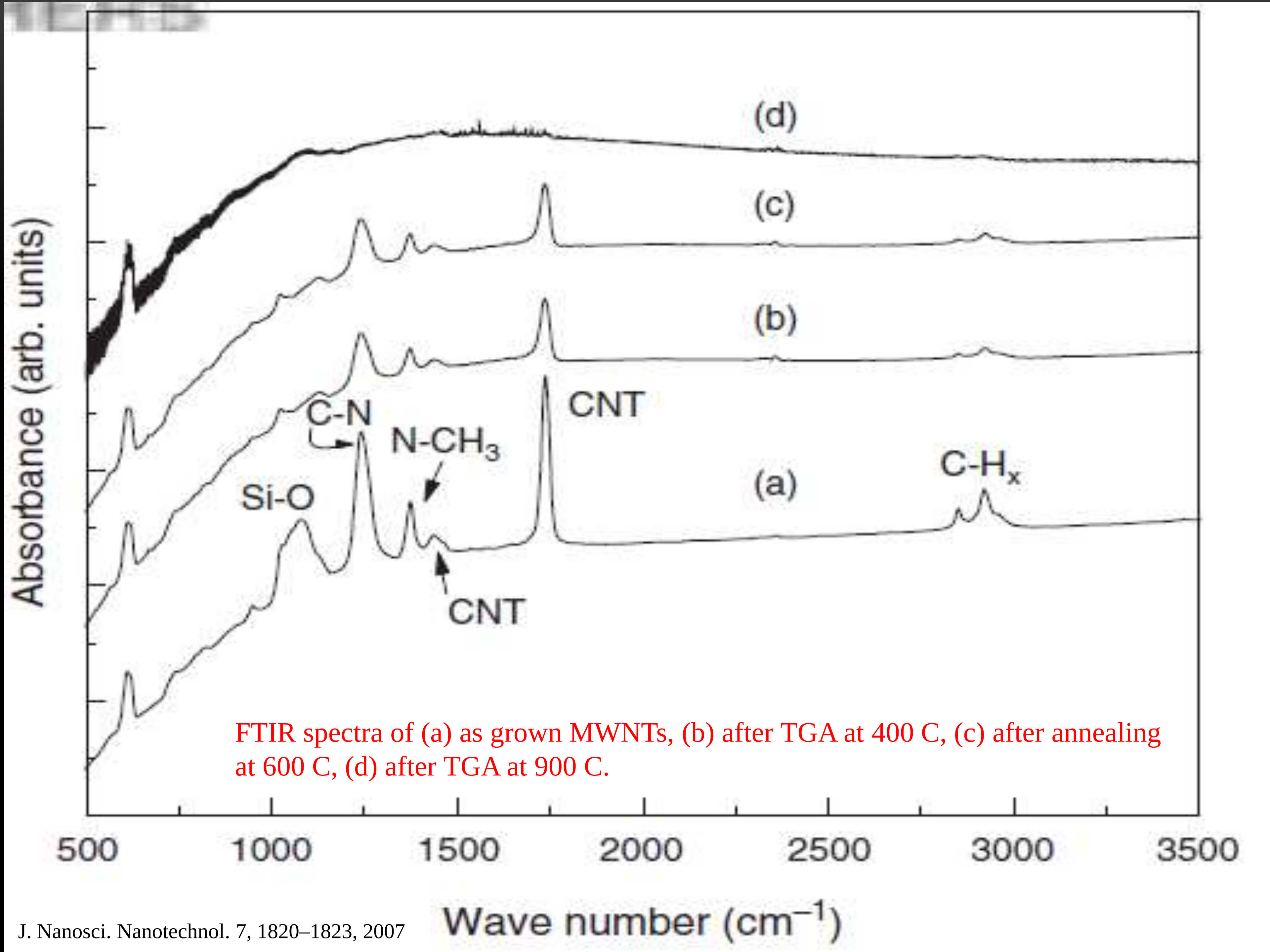


Beilstein J. Nanotechnol. **2016,** *7*, 1822–1828.

Multi-Walled Carbon Nanotubes

- The presence of defects and impurities that are electronically and chemically active can change effectively the properties of carbon nanotubes (CNTs).
- Nitrogen (N) doping into carbon layers is one of the effective approaches to modify these properties, as the controlled electrical properties are very important in electronic devices at nanoscale.



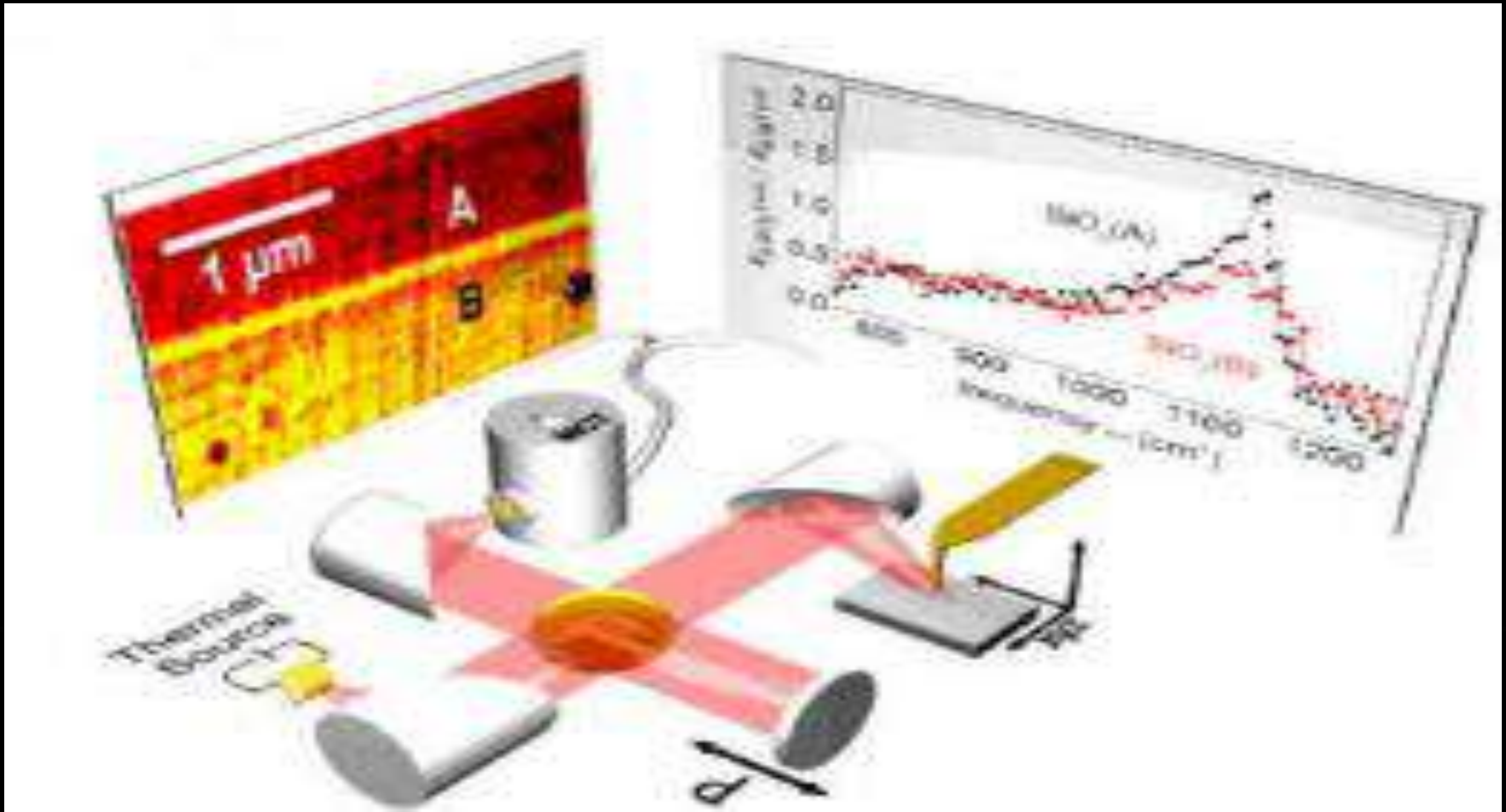


FTIR spectra of (a) as grown MWNTs, (b) after TGA at 400 C, (c) after annealing at 600 C, (d) after TGA at 900 C.

J. Nanosci. Nanotechnol. 7, 1820–1823, 2007

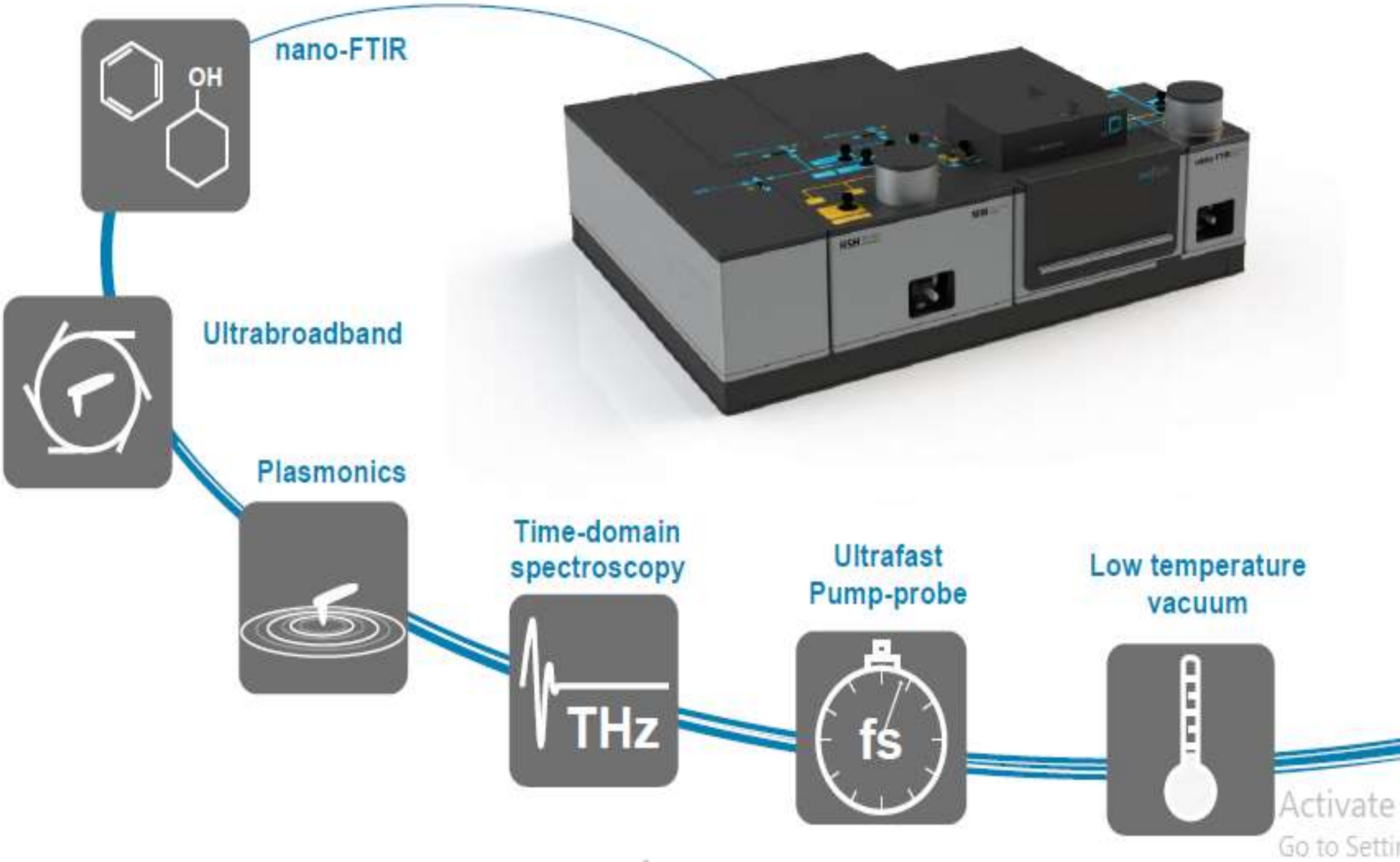
Nano-FTIR with a Thermal Source

- Infrared nano-spectroscopy with a thermal source. The tip is illuminated with the broadband infrared radiation from a thermal source and the backscattered light is analyzed with a Fourier spectrometer, yielding local infrared spectra with a spatial resolution better than 100 nm.



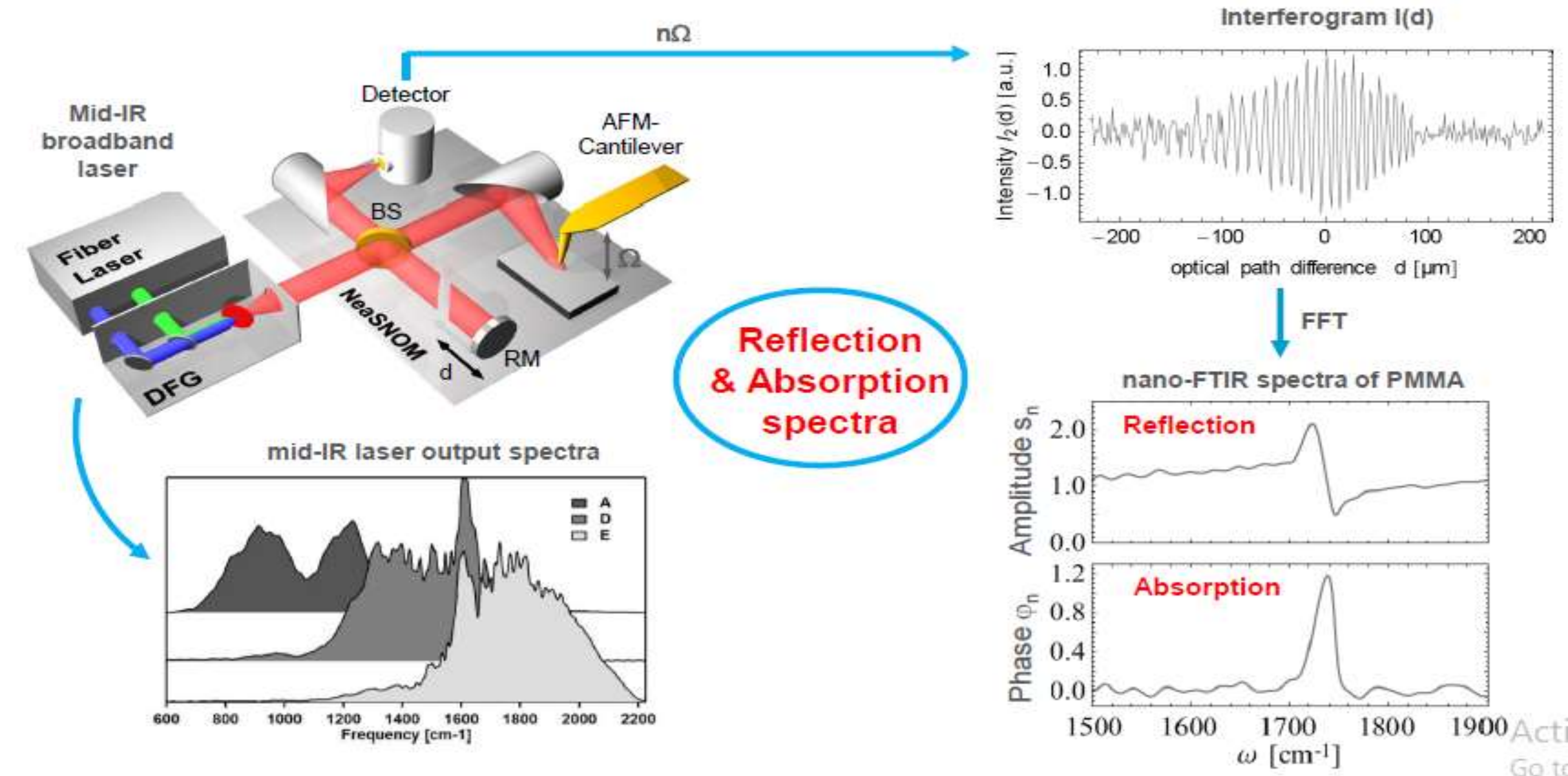
- Researchers from the Basque nanoscience research center (Germany) have developed an instrument that allows for recording infrared spectra with a thermal source at a resolution that is 100 times better than in conventional infrared spectroscopy. The technique could be applied for analyzing the local chemical composition and structure of nanoscale materials in polymer composites, semiconductor devices, minerals or biological tissue.
- Based on vibrational fingerprint spectroscopy, it could be applied for nanoscale mapping of chemical composition and structural properties of organic and inorganic nano-systems, including organic semiconductors, solar cells, nanowires, ceramics and minerals.

Nano-FTIR


nano-FTIR
OH
Ultrabroadband
Plasmonics
Time-domain spectroscopy
THz
Ultrafast Pump-probe
fs
Low temperature vacuum

IR is highly sensitive to:

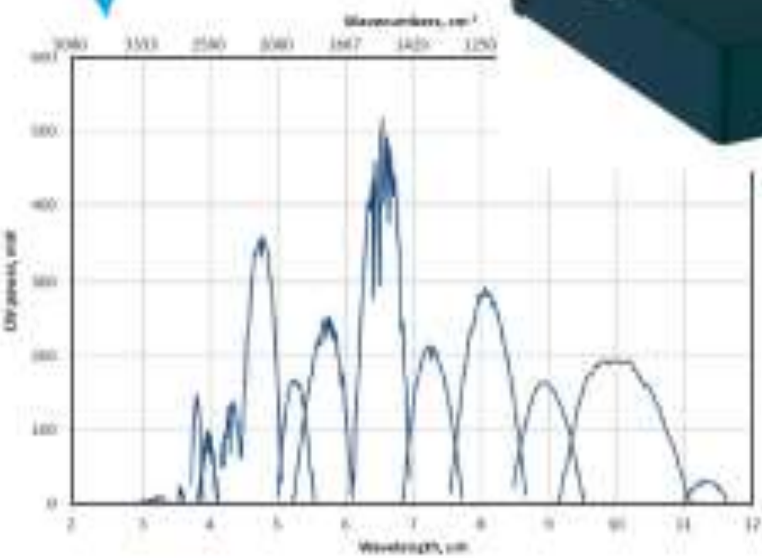
- Molecular vibrations → Chemical composition
- Crystal lattice vibrations → Structural properties
- Plasmons in doped semiconductors → Electron properties



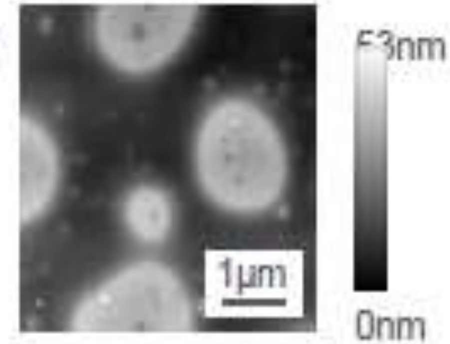
neaSNOM enables 2D near-field imaging (chemical mapping) with reflection & absorption information

Interferometric detection

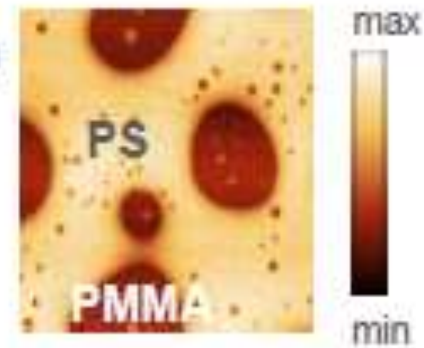
© Daylight solutions



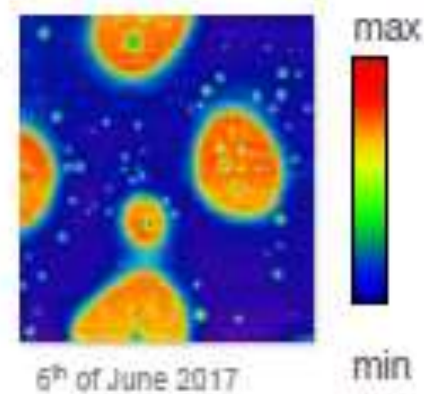
Topography



Reflection



Absorption

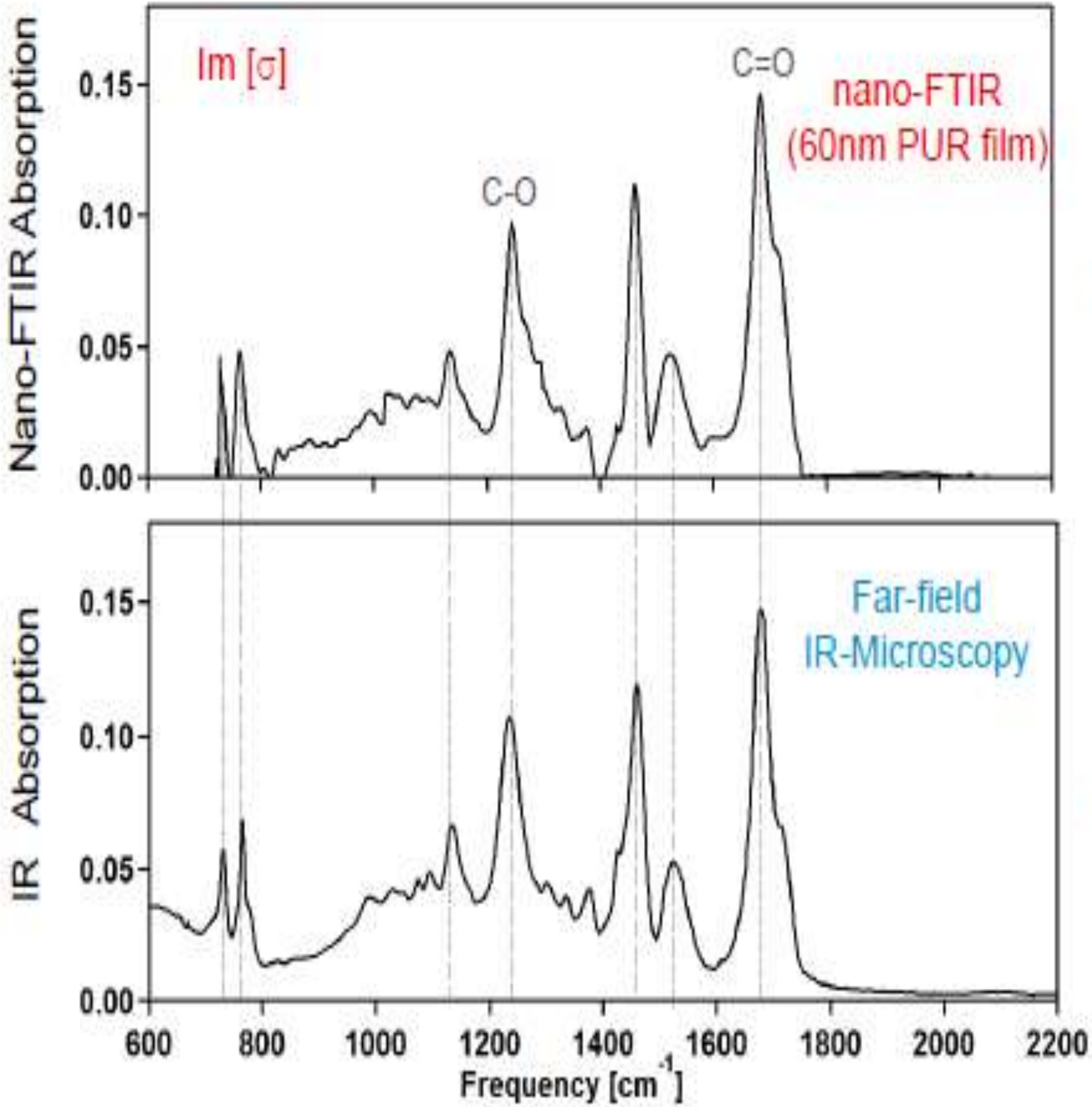


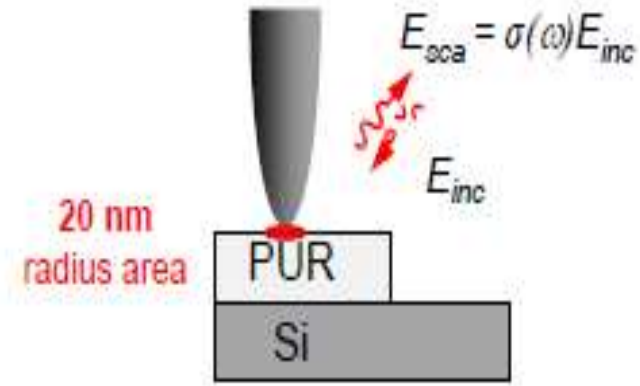
<u>Scan parameters:</u>
ω=1740cm⁻¹ (λ=5.75µm)
Time constant (Lock-In): **0.52ms**

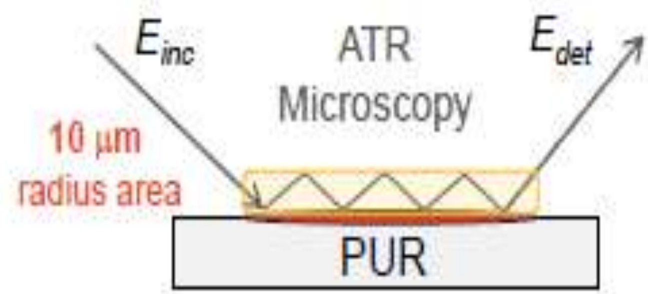
6th of June 2017

nea spec

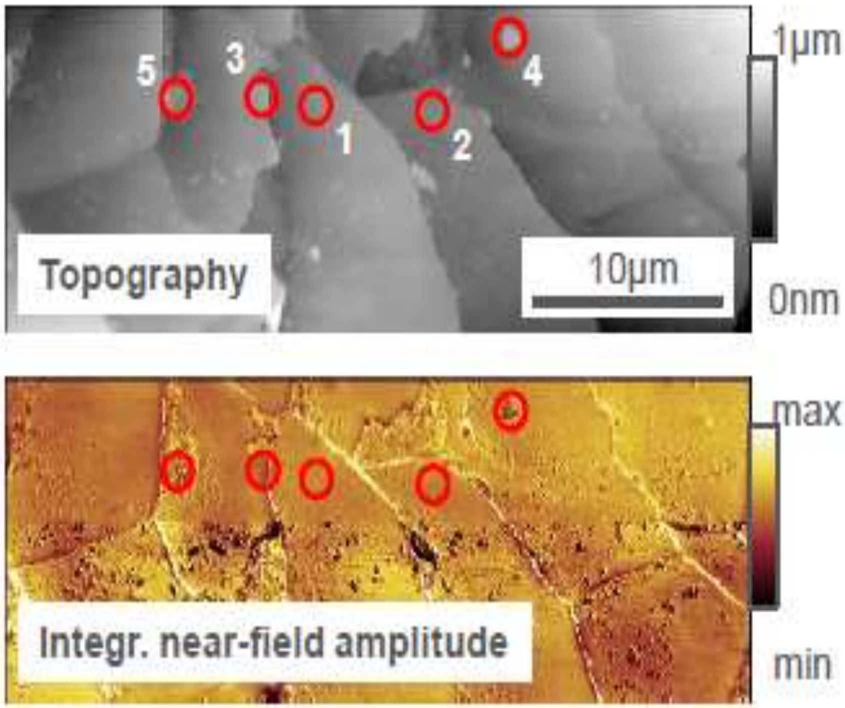
Comparing nano-FTIR and conventional far-field IR







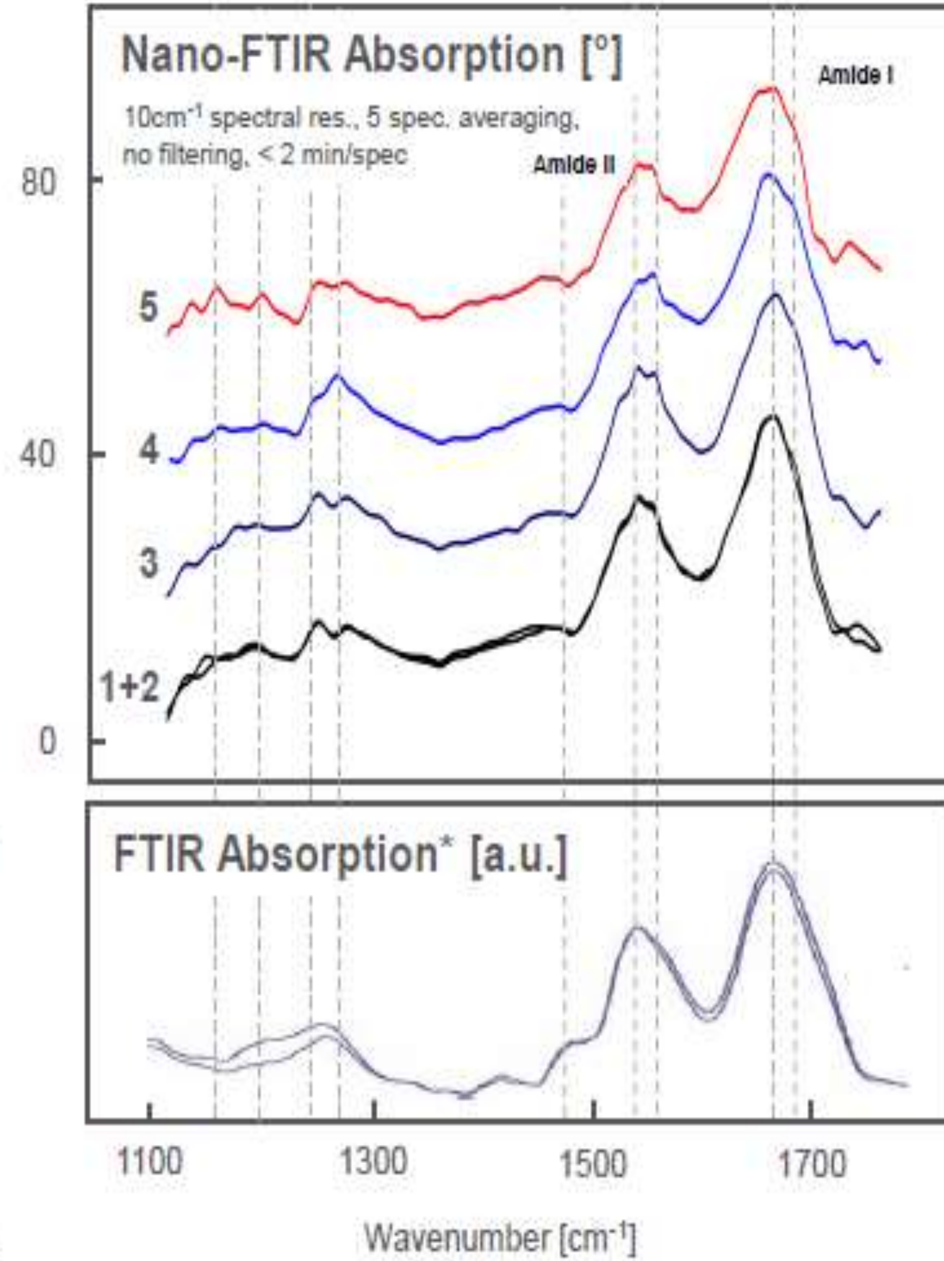
characteristic hair IR absorption spectrum at selected locations



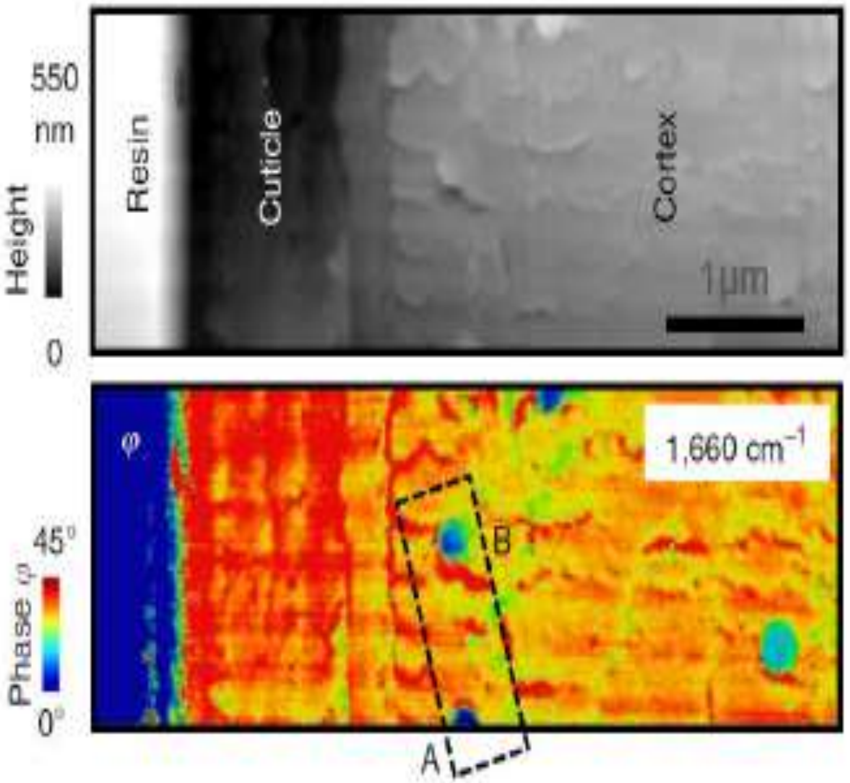
nano-FTIR spectra show charararacteristic absorption signatures (Amide I +II) similar to far-field FTIR

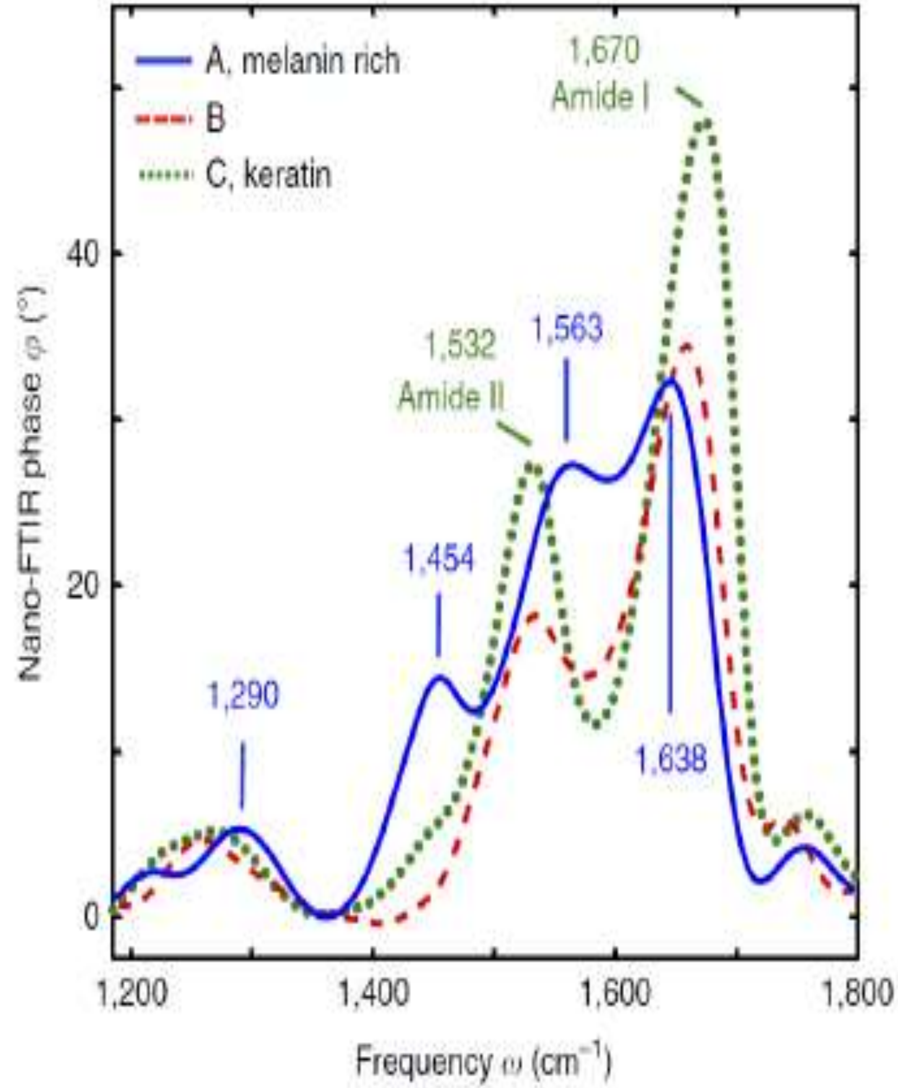
Excellent reproducibility (spectra 1+2);
Small variation at selected locations (spectra 3+4)

Red spectrum indicates additional lipid signature



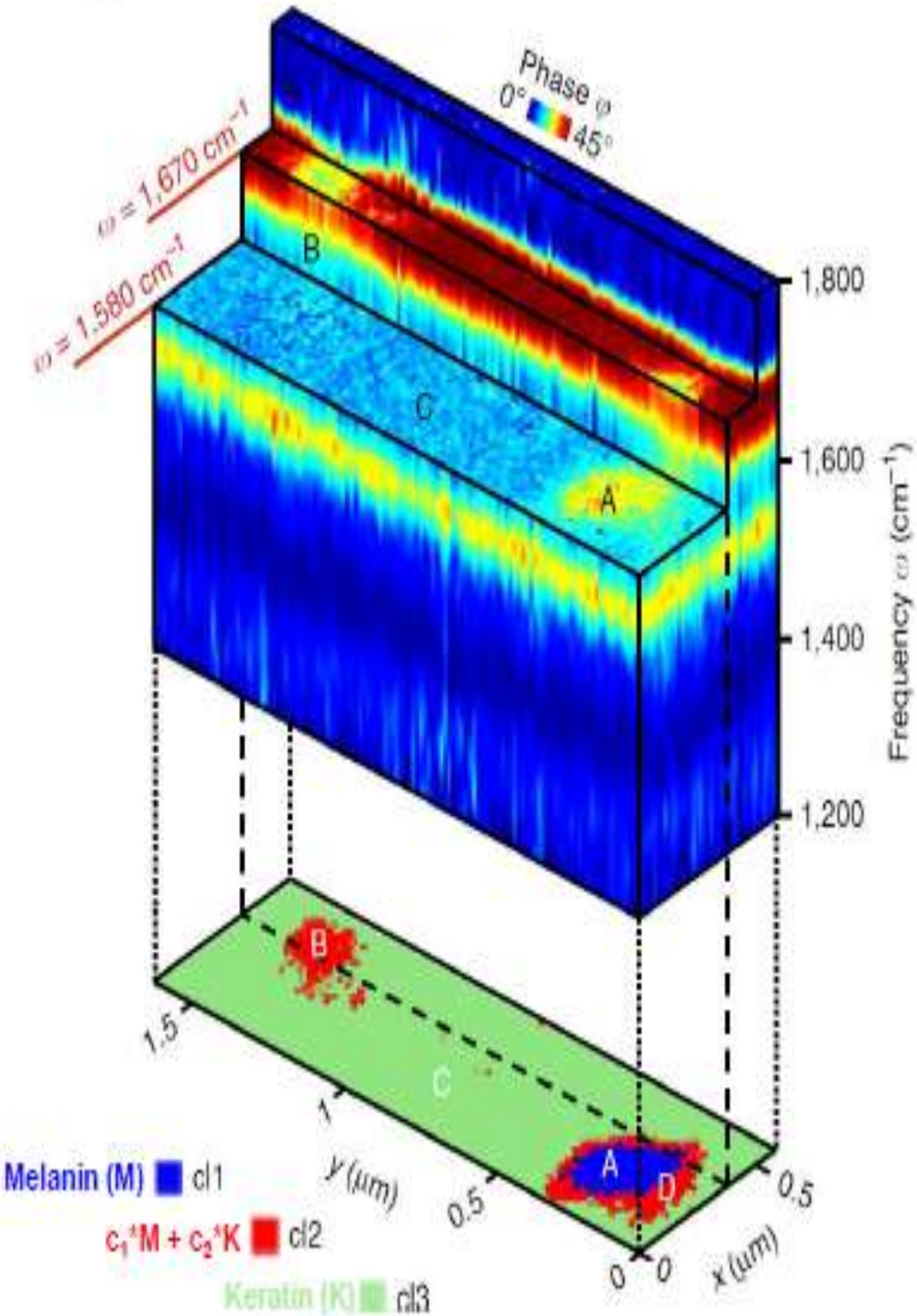
Hair cross section:



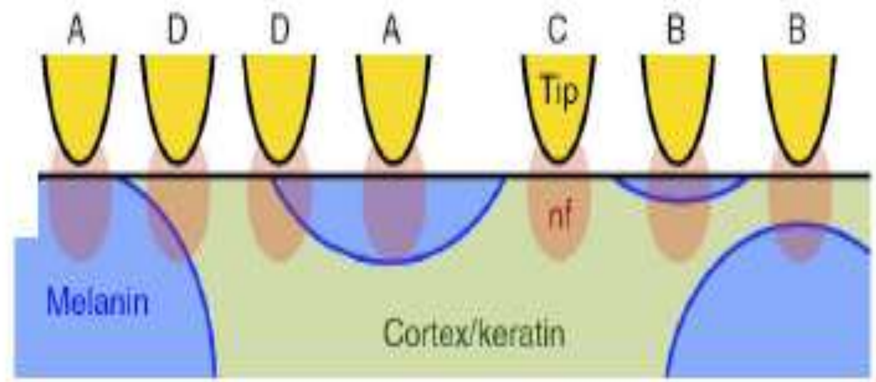


- Hair cross section: nanoscale IR imaging at 1660cm^{-1} reveals disk shaped ca. d=300nm dark areas at 1660cm^{-1} in cortex region
- nano-FTIR verifies inclusions as **melanin-rich areas**

I. Amenabar, et al., *Nature Comm. 8*, 14402 (2017)

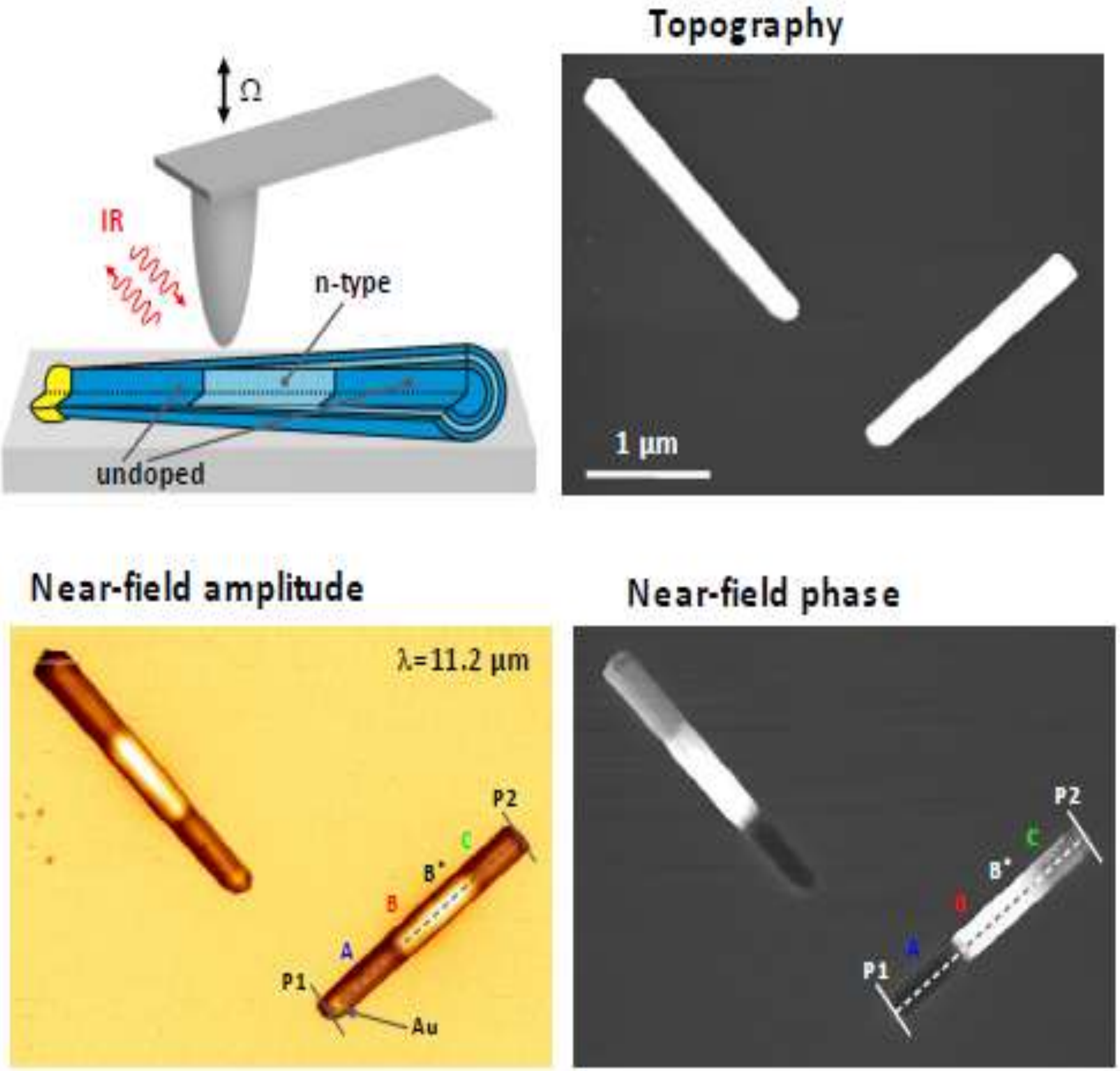


- nano-FTIR hyperspectral imaging with full spectroscopic signature at every pixel of imaged area
- Analysis of spectral signatures enables to identify
  - pure cortex/keratin areas (C)
  - pure melanin areas (A)
  - mixed phase (B,D)
- Mulitvariate data analysis reveals three clusters of materials (segmentation map)



I. Amenabar, et al., *Nature Comm. 8*, 14402 (2017)

s-SNOM can directly measure the local carrier densities in nanoparticles/-wires



J. M. Stiegler et al., Nano Lett. 10, 1387 (2010)

- InP nanowires with modulation in doping concentration
- Center segment features highly conductive properties at 11.2µm wavelength
- Detection of doping gradient between adjacent sections
- Contact-free determination of doping concentration from near-field scans
- Mid-IR s-SNOM is sensitive to free charge carrier concentrations between ca. $10^{18} – 10^{20}$ cm^{-1}


Thank you